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Some Relations between the Chemical Constitution of Cibacron Dyes and their Dyeing Characteristics

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One-day Symposium on "Reactive Dyes" held by the Manchester Section at the Manchester College of Science and Technology on 20th March 1959, Mr. J. W. Reidy in the chair

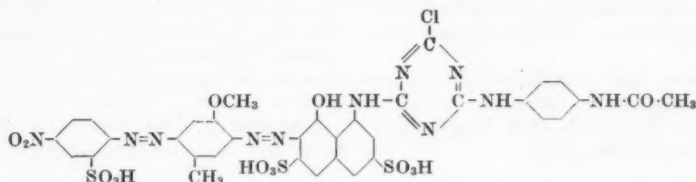
The early history of the reactive dyes and the requirements for practical application are discussed. The structural elements of Cibacron reactive dyes are indicated, and the dyeing properties of such dyes of the azo, anthraquinone and phthalocyanine groups are correlated with their chemical constitution. Reference is made to the advantage of using a special detergent for washing off reactive dyeings produced with phthalocyanine derivatives.

INTRODUCTION

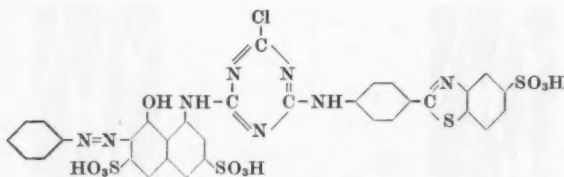
The reactive group of the Cibacron dyes is a monochlorotriazine residue which reacts with the hydroxyl group of the cellulose to bring about true chemical fixation. Dyes containing this grouping have been on the market for more than 30 years as members of Ciba's direct range¹, e.g.—

order to understand them it is necessary to recall the views relating to the mechanism of the dyeing process which were current about 1930.

The first to synthesise dyes of the cyanuric chloride, reactive type within the cotton fibre was Haller, who was one of the originators of the theory of the optimum degree of dispersion². According



Chlorantone Fast Blue 8G



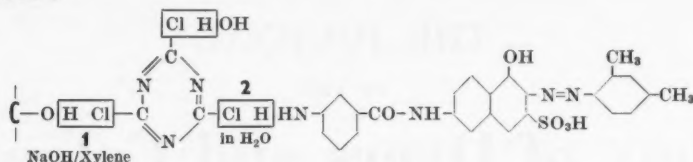
Direct Brilliant Pink G

It is really most surprising that it took so long for a reactive dye range as such to come into being, especially when we consider the fact that dyeings based on covalent combination of dye and substrate were produced long ago by synthesis within the cellulose². Cyanuric chloride was used, and the two alternative series of reactions were as on p. 206.

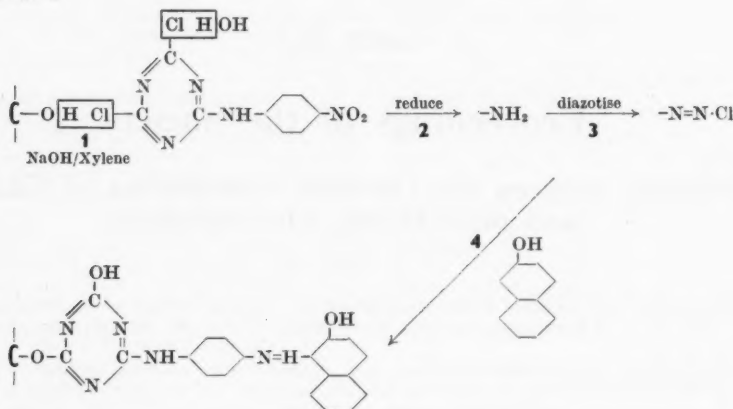
The reasons for this slow development are important enough to merit a brief discussion. In

to this theory, direct dyes are taken up and retained by cellulosic fibres only when they are in the form of colloidal particles of just the right dimensions to have access to, and be retained in, the inter-micellar spaces of the cellulose. This theory, and the belief that cellulose was chemically inert, explains why the step from synthesis in the fibre to the direct application of a reactive dye of the chlorotriazine type (which was then already

Series 1



Series 2



available) was not undertaken. It was not until Boulton and Morton⁴ had completed their fundamental work that these views were refuted. By clearly establishing the molecular theory of cellulose dyeing, they laid the foundations for the final development of the reactive dyes. In fact it is difficult to imagine penetration of the fibre by colloidal particles comprising hundreds of dye molecules. Only single molecules are capable of being adsorbed by the cellulose in a manner which allows them to react with it. The two theories are illustrated in Fig. 1.

Reactive dyes are first adsorbed similarly to direct dyes and show positive dichroism, i.e. they are deposited in the fibre with their longitudinal axis parallel to the cellulose chains.

Although chlorotriazine dyes have been known for a long time, it must not be thought that, in order to build up the Cibacron range, all that had to be done was to make a selection of existing products. Not only did a great deal of work have to be done on the application side: the Ciba dyestuff research chemists had to make a very considerable contribution. Although every dye containing a monochlorotriazine ring is a reactive dye, not every monochlorotriazine dye is a Cibacron. The object of this paper is to discuss in detail the general formulation, and to relate the requirements of practical application to the various possibilities open in respect of chemical constitution.

Cibacron dyes are not characterised by the fact that they have certain constitutional features in

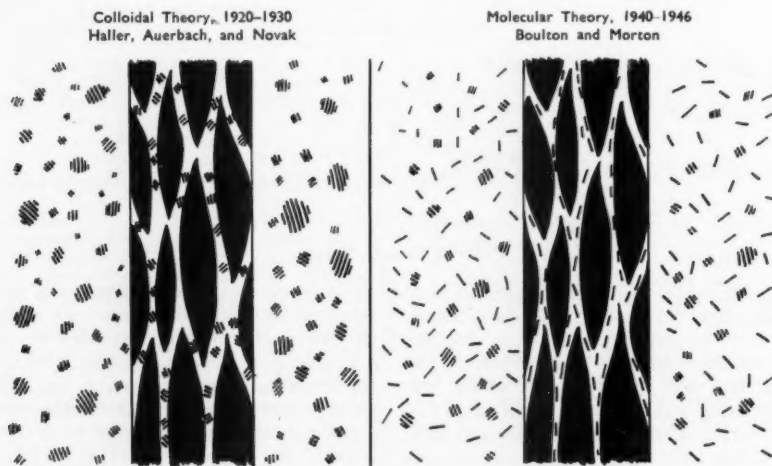


FIG. 1—Theory of Cellulose Dyeing

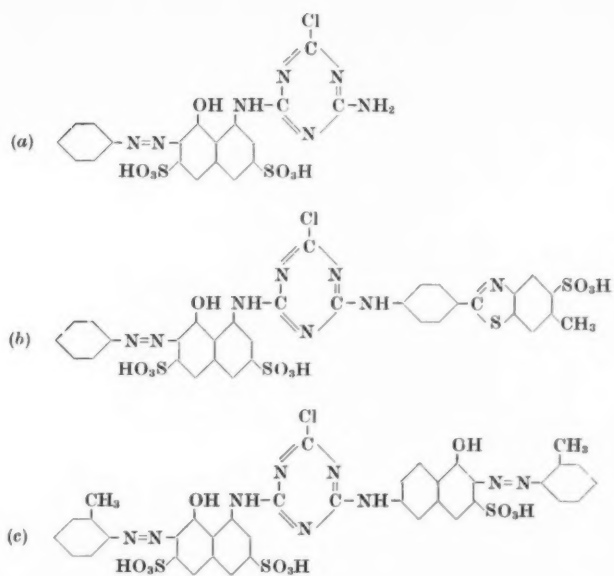
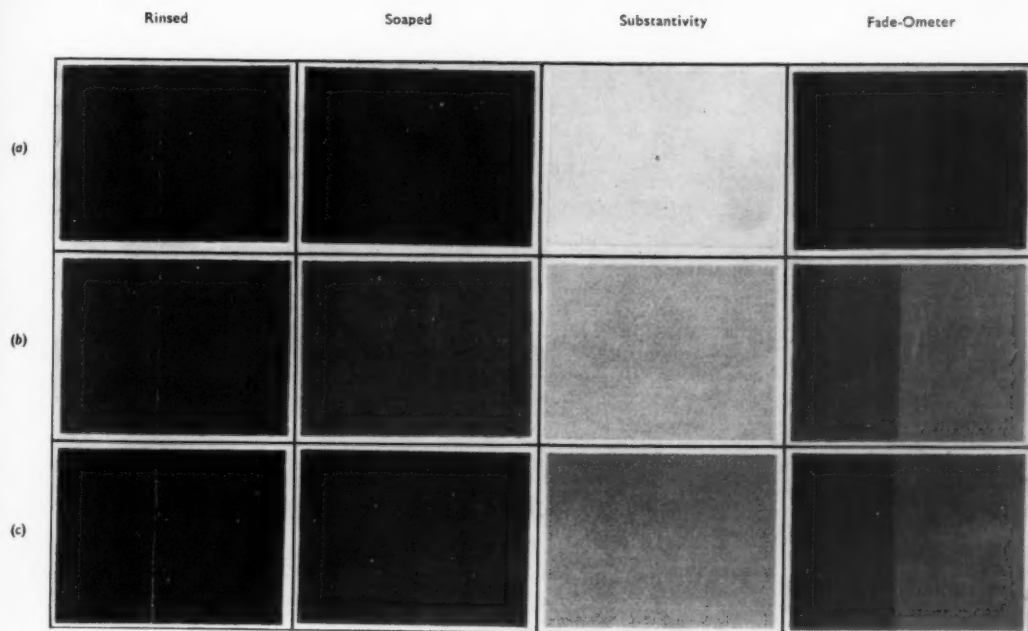


FIG. 2—Effect on Substantivity and Light Fastness of Substituents in the Triazine Ring

	30 sec.	Pad-Steam	120 sec.	Substantivity	Water test	
(a)						Distilled water
						Hard water
(b)						Distilled water
						Hard water

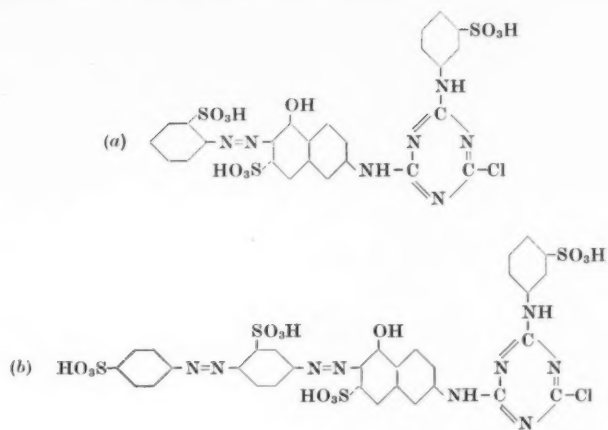
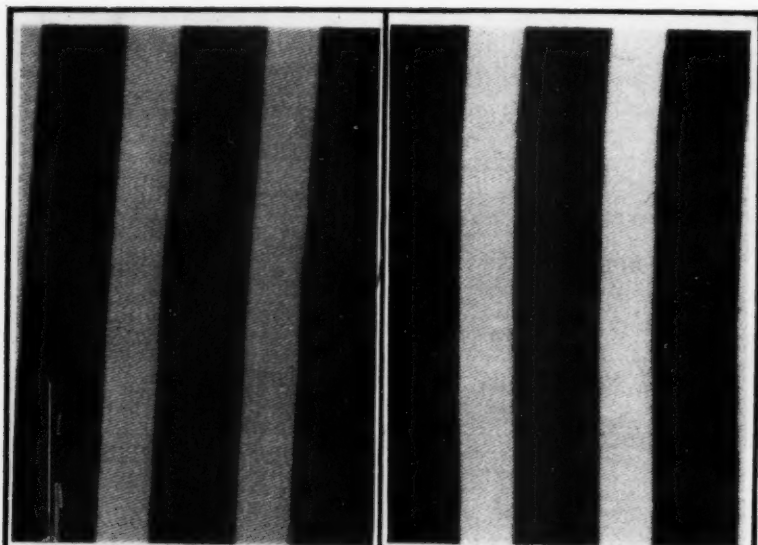


FIG. 4—Substantivity of Monoazo and Disazo Dyes

(a)



(b)

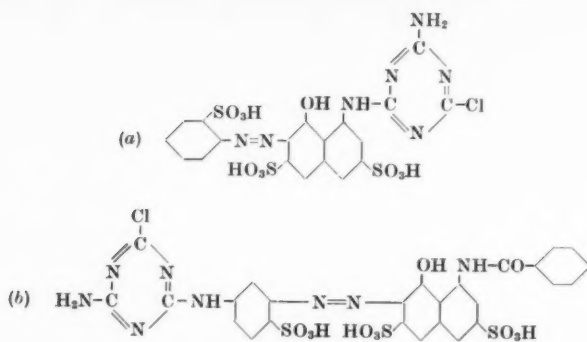
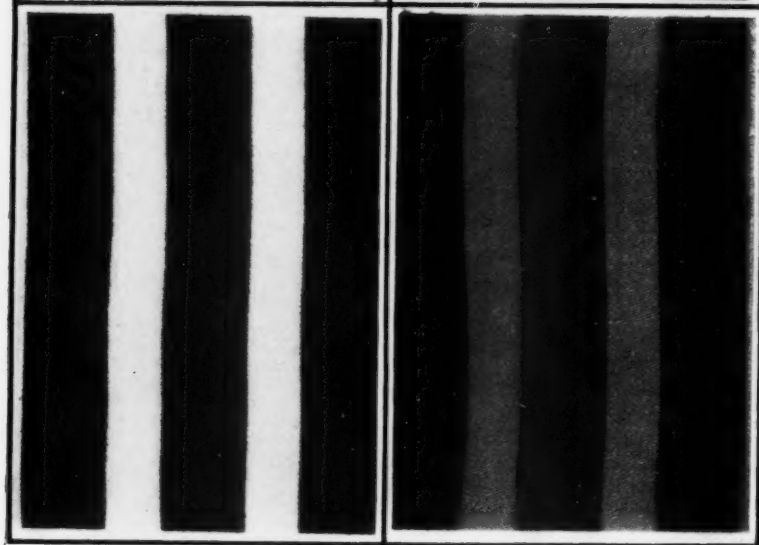
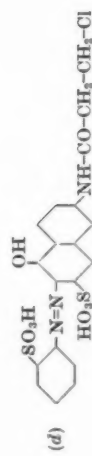
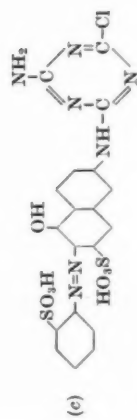
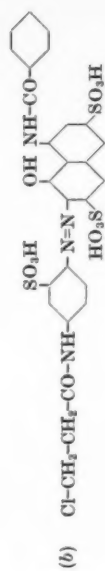
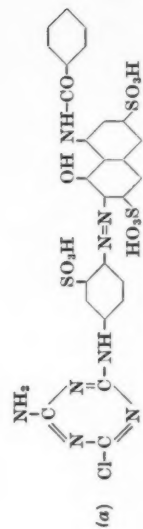


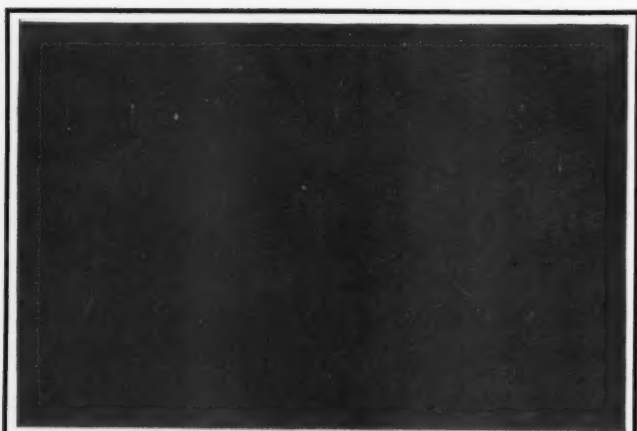
FIG. 5 - Effect of Position of Reactive Group on Dischargeability



Hue	Substantivity	
	Distilled water	
	Hard water	
	Distilled water	
	Hard water	
	Distilled water	
	Hard water	
	Distilled water	
	Hard water	

Fig. 6—Effect of Chemical Constitution on Hue and Substantivity

(a)



(b)

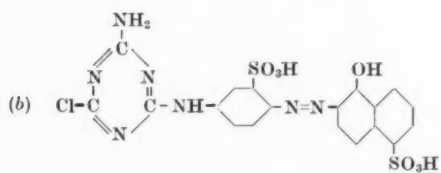
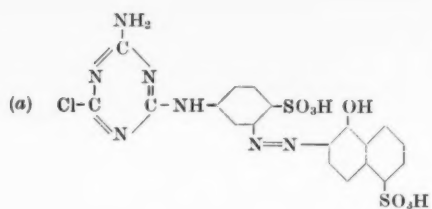


FIG. 7—Effect on Hue of the Position of the Cyanurated Amino Group

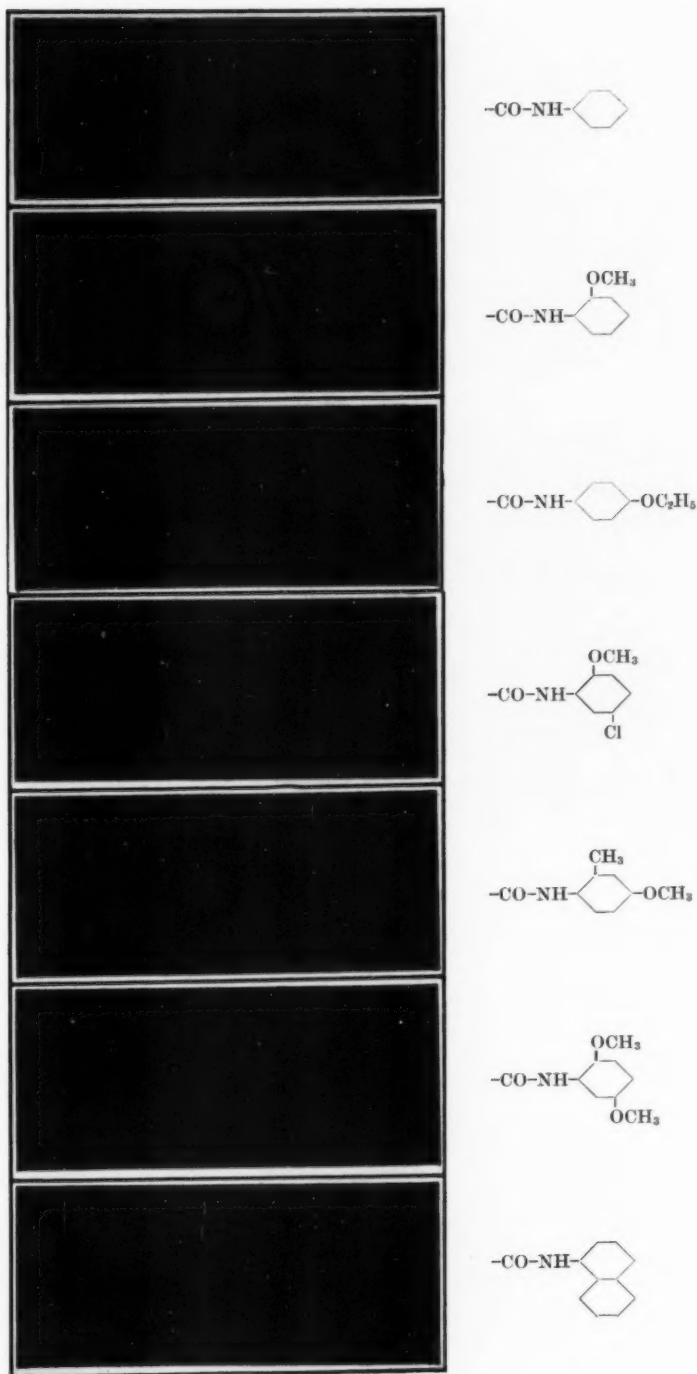
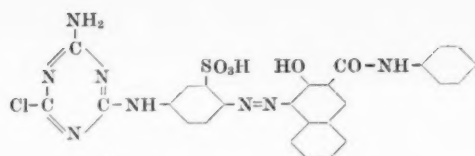
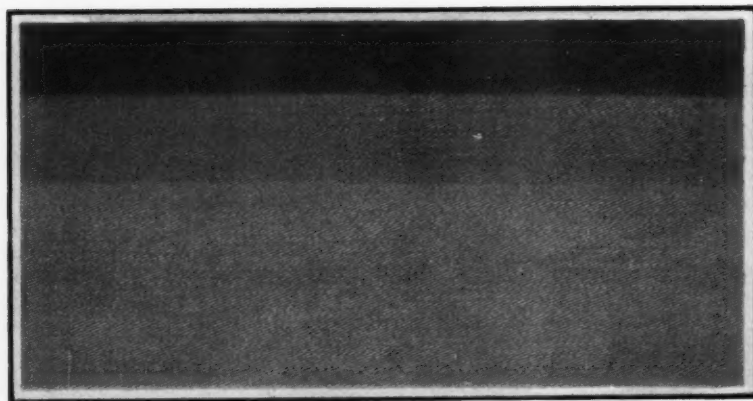


FIG. 8—Similar Effect of Different Azole Coupling Components

Fade-Ometer

(a)

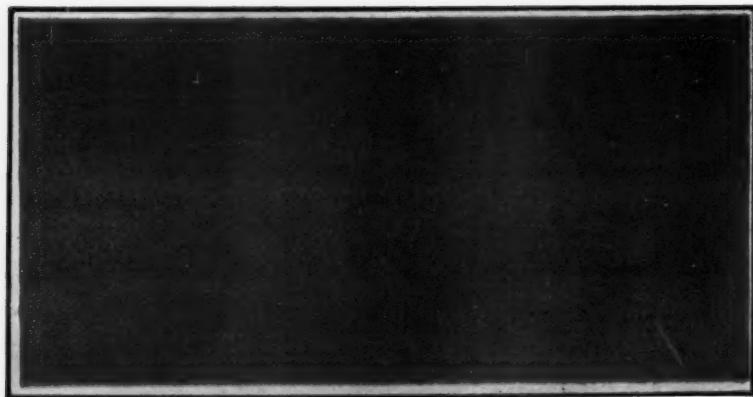


Exposure
(hr.)
20

60

160

(b)



Exposure
(hr.)
20

60

160

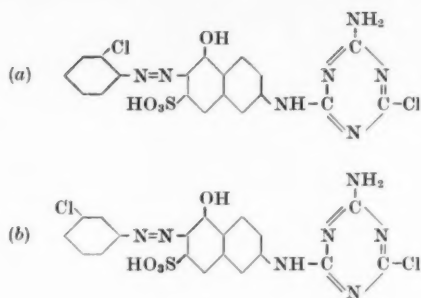


FIG. 9—Effect on Light Fastness of Position of Cl Atom

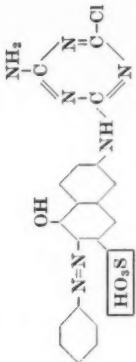
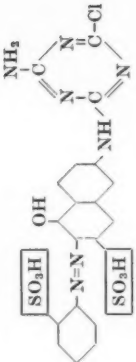
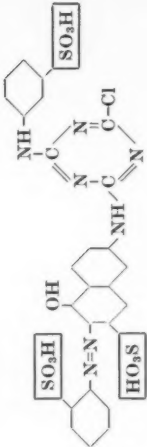
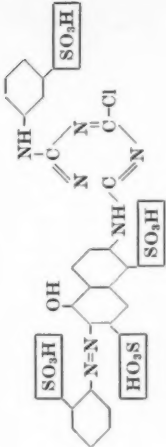
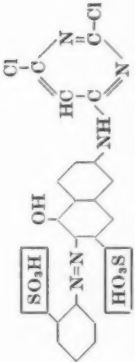
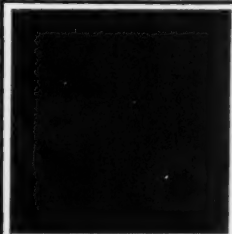

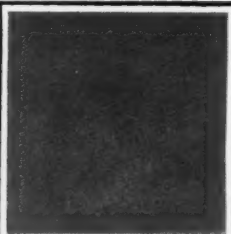
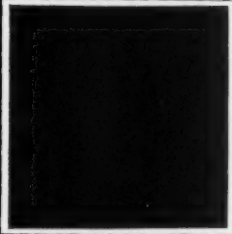

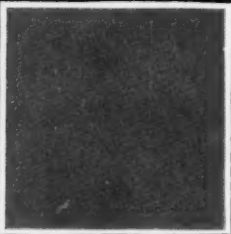
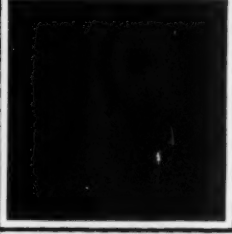

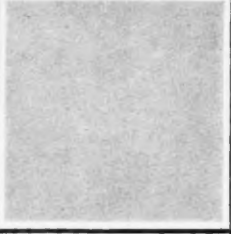
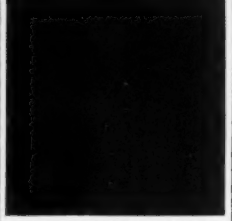


	Dyeing	Distilled water	Substantivity	Hard water
 <p>(a)</p>				
 <p>(b)</p>				
 <p>(c)</p>				
 <p>(d)</p>				
 <p>(e)</p>				

FIG. 10.—Effect of ((a)–(d)) Increasing Sulphonation and (e) a Pyrimidine Ring on Substantivity

	Hue	Distilled water	Substantivity	Hard water
(a)				
(b)				
(c)				
(d)				

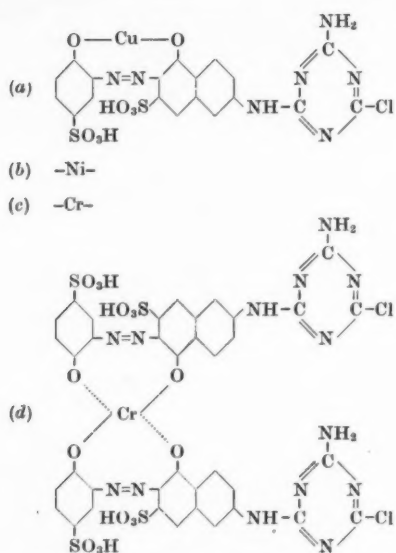


FIG. 11—Hue and Substantivity of 1:1 and 2:1 Metal-complex Dyes

	Hue	Acid	Hydrolysis (4 hr.)	Alkaline
(a)				
(b)				

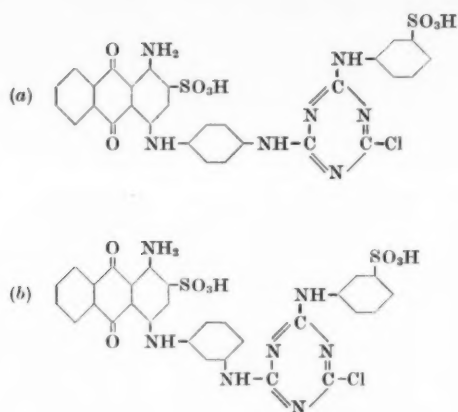


FIG. 12—Effect on Hue of the Position of the Cyanurated Amino Group

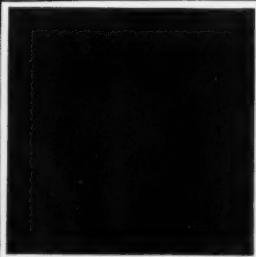
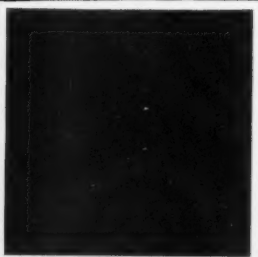
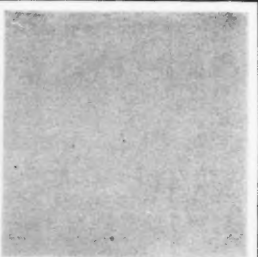


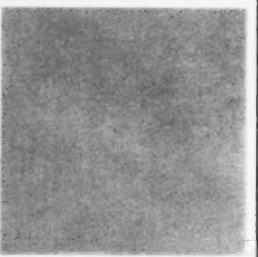
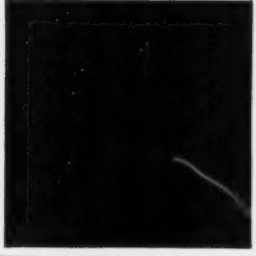
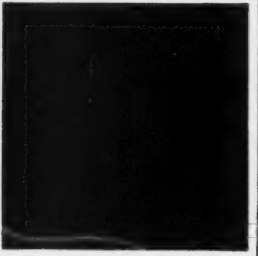
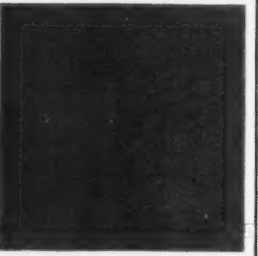


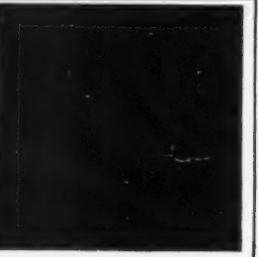
Padded, dried, and baked	Rinsed	Soaped	
			$\begin{array}{c} \text{--SO}_2\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \\ \text{HO}_3\text{S}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2 \end{array}$
			$\begin{array}{c} \text{--SO}_2\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \\ \text{HO}_3\text{S}\cdot\text{O}\cdot\text{CH}_3 \end{array}$
			$\begin{array}{c} \text{--SO}_2\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \\ \text{HO}_3\text{S}\cdot\text{O} \end{array}$
			$\begin{array}{c} \text{--SO}_2\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \\ \text{Cl} \end{array}$

Fig. 13.—Reactive Dyes from Cu-Phthalocyaninetetra-sulphonic Acid

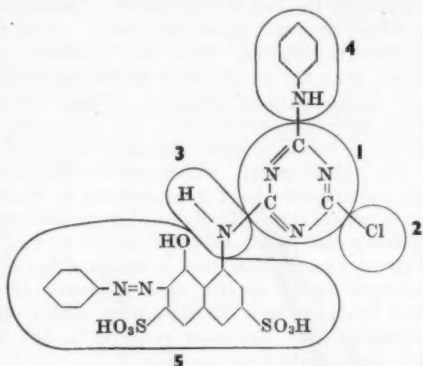
common, e.g. a chlorotriazine ring, but rather by their dyeing properties. It is therefore quite possible for the range to include dyes with other reactive groups. However, this has not yet been the case, so this paper is restricted mainly to the monochlorotriazine dyes, and in particular to the dyeing of cellulose, since other criteria apply to the dyeing of wool.

REQUIREMENTS OF PRACTICAL APPLICATION

The two fundamental systems of coloration are application by exhaustion and application by impregnation through padding or printing, and each makes different demands on the dyes. In the batchwise exhaustion method the dye molecules, on account of their substantivity, leave the aqueous bath and diffuse into the fibre where they are fixed, whereas, in padding or printing, they are applied mechanically to the site where fixation is to take place. It is essential that dye which is not chemically fixed to the fibre should be completely washed off fairly soon after application. It is thus evident that one of the main requirements is a well-balanced substantivity, i.e. the substantivity of the dye should not be too low and, what is more important, not too high. Another essential is that the yield, i.e. the amount of dye which reacts with the fibre, should be as high as possible; this depends partly on the substantivity and partly on the reactivity of the dye. The speed at which a dye reacts is also an important factor. Other factors which have to be taken into account when making a final selection (and which sometimes justify an exception being made) are the stability of the dye in substance, in solution, during reaction with the fibre, and in the fibre, i.e. the stability of the linkage. In addition, there are the usual requirements with regard to fastness properties, hue, tinctorial strength, and brilliance.

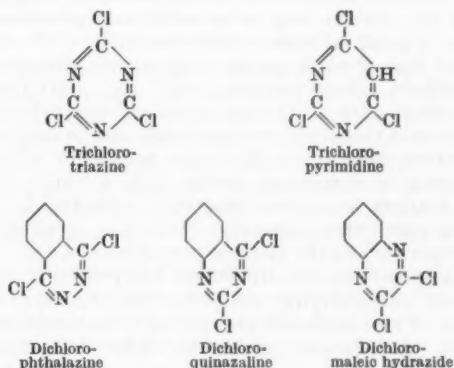
STRUCTURAL ELEMENTS OF CIBACRON DYES

The general structure of a monochlorotriazine dye can be divided into 5 main constituents which, to a differing degree, offer many possibilities of variation. These constituents, which will next be examined separately with regard to their relative significance and their influence on dyeing characteristics, comprise: the triazine ring (1), the exchangeable reactive group (2), the bridge to the dye molecule (3), a further substituent of the triazine ring (4), and the dye molecule itself (5)—



(1) The Triazine Ring

The function of the trichlorotriazine or cyanuric trichloride ring is to link the other substituents together. This ring permits of only a few variations, e.g.—



but in some cases these can have a considerable influence on the properties of the dye. As Haller showed, a fused ring such as dichlorophthalazine, dichloroquinazoline or dichloromaleic hydrazide can be used. It is also possible to replace a nitrogen atom of the triazine ring with a CH group, which gives trichloropyrimidine. The reactivity of a dye containing this group is generally lower than that of the corresponding dye containing the triazine ring.

(2) The Reactive Group

In accordance with the general rule that the larger the diameter of a halogen atom, the more readily it is split off, reactivity increases in the following order: F, Cl, Br, I. The chlorine atom is given preference, since in respect of price and exchangeability, it is roughly mid-way between the others.

It is also possible to use other substituents as cleavable groups in place of halogen atoms, e.g. a sulphonic group or a pyridinium halide, but as a rule no advantage is gained. A pyridinium salt, for example, does not bring about a quicker reaction. Moreover, it reduces the solubility of many dyes in an alkaline solution to such an extent—through the formation of zwitterions—that the possibilities of application are considerably limited. The resulting dyeing is always the same, irrespective of the type of cleavable group used, so all that has to be taken into account is the influence of the group on the rate of reaction and the solubility of the dye.

(3) Linkage of the Dye Molecule to the Triazine Ring

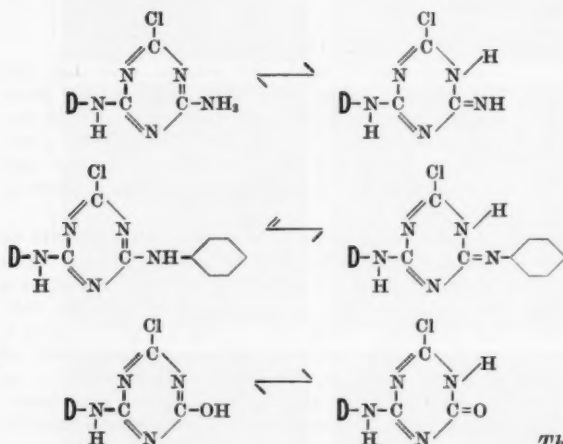
The group chosen to link the triazine ring with the dye molecule is of great importance, as regards both the stability of the dye and its reacting capacity. Oxygen and sulphur bridges generally result in dyes which are less stable towards alkaline hydrolysis, which leads to undesirable side-reactions in some methods of application, e.g. in pad-steam dyeing. They are also less easy to synthesise than the NH bridge. Substitution of this group by alkylation results in increased

stability of the linkage, but it has the disadvantage of reducing the rate of reaction, so this variation is only usable within certain limits.

(4) Further Substituents of the Triazine Ring

It is well known that a chlorine atom, when left on the triazine ring as an additional substituent, has a great influence on the reactivity of the dye, and that a whole group of dyes with completely different characteristics, viz. the cold-dyeing Procion dyes (ICI), are based on this principle. The fact that a coloured molecule can be used as a further substituent offers the possibility of producing a compound shade with a single dye. Colourless, so-called "inactive" substituents can influence very strongly both the application properties and the fastness properties of a dye. In many cases such a substituent has proved of great value in modifying the properties of a dye, e.g. one or two sulphonic groups can be substituted in the phenylamino group in order to increase solubility.

Taking a number of simple substituents in the triazine ring, starting with phenyl, hydroxy, methoxy, phenoxy, amino, phenylamino, hydroxyethylamino, dihydroxyethylamino, etc., it can be said that the reactivity of a dye decreases approximately as the basicity of the substituents increases. However, one factor has to be given due consideration, viz. the tendency to change into the tautomeric form—



It is probably for this reason that an OH group produces dyes which are very slow to react, whereas the OCH_3 group, and also the phenyl group, give dyes which are very highly reactive. The higher basicity of the aniline derivative compared with the amino-substituted compound is probably also attributable to the fact that the latter has a greater tendency to change into the tautomeric form. However, the difference in reactivity between amino and phenylamino is slight compared with hydroxy and phenoxy. Hydroxy-chlorotriazine dyes, as well as ethylamino- and diethylamino-chlorotriazine dyes, generally react too slowly to be applicable by the continuous methods for which the Cibacrons are so well suited—the fixation times are too short. Compounds such

as dehydrothio-*p*-toluidinesulphonic acid (Fig. 2 (b)) give increased substantivity, but reduce the light fastness.

Reduction in light fastness can also be caused by the use of a coloured molecule as a further substituent (Fig. 2 (c)), so all the factors have to be given very careful consideration when selecting usable dyes built up on this basis. In addition, a reduction in yield must be expected when two dye molecules of the same type are linked together (Fig. 3), i.e. more of the dye will react with water and less with the fibre.

(5) The Dye Molecule

Several thousand combinations can be created simply on the basis of the variations possible with the four structural units discussed above. When it is also considered that every coloured substance applicable as a dye can in some way or other be endowed with a reactive group and used as a reactive dye, some idea is gained of the almost unlimited possibilities. This paper, however, is restricted to those molecules which contain ionisable, anionic solubilising groups, i.e. those which could be used as Cibacrons. The discussion is further limited to three groups, viz. the azo, anthraquinone, and phthalocyanine derivatives.

AZO DYES

Monoazo dyes are the most important members of this group. Disazo dyes have the disadvantage of being much more sensitive to reduction and many of them exhibit a degree of substantivity which does not allow the hydrolysed dye to be washed off completely in bulk practice (Fig. 4).

The position of the reactive group is responsible for the important difference in the case of the azo dyes. If the group is in the diazo component the dyeing can be discharged to white, but not if it is in the coupling component, because coloured decomposition products remain in the fibre (Fig. 5). Recognition of the type of dye is simple. If the reactive group is in the diazo component, the same dye can be re-formed by diazotising and coupling the discharged dyeing; this cannot be done if the reactive group is in the coupling component (Fig. 5).

The Chlorotriazine Residue in the Diazo Component

It is mainly the yellow to violet dyes in the colour range which are built up on this basis. Apart from their dischargeability, they also exhibit good stability, since the cyanurated amino group shows a fairly high degree of basicity. When compared with a chloropropionyl dye, for example, the difference in hue is considerable (Fig. 6 (a) and (b)), since the amino group, which carries the reactive group, participates to a great extent in the conjugation, whereas practically no change in hue takes place in the case of a J-acid dye (Fig. 6 (c) and (d)).

Of great importance, too, is the position of the cyanurated amino group; this is shown by the marked hypsochromic displacement which occurs on changing from the *para* position to the more weakly basic *meta* position (Fig. 7).

In contrast, substitution in the coupling component has in some cases almost no effect. Thus, all combinations made with azoic coupling components which are derivatives of naphthalene surprisingly enough produce practically the same colour (Fig. 8).

The Chlorotriazine Residue in the Coupling Component

It is mainly the orange to violet dyes which are built up on this basis. The choice of the diazo component is extremely important. For example, the light fastness of a cyanuric chloride-J-acid dye can be reduced from 5 to 1 if *o*-chloroaniline is used instead of *m*-chloroaniline (Fig. 9).

These dyes generally show a fairly high degree of substantivity and are therefore difficult to wash off. The substantivity can be reduced considerably by introducing more sulphonic groups, but this can give rise to some undesirable side-effects. For example, it is undesirable to have a sulphonic group *ortho* to the cyanurated amino group (Fig. 10 (d)), since it markedly reduces the stability of the dye—presumably because it reduces the basicity by forming an internal salt linkage with the NH bridge. There are other methods of reducing the substantivity apart from increasing the number of sulphonic groups, and some of them are much more effective. For example, by replacing the triazine ring of a disulphonated dye with a pyrimidine ring (Fig. 10 (e)), the substantivity can be depressed to about that of the tetrasulphonated dye.

METAL-COMPLEX DYES

It is known from the direct dyes that copper complexes tend to possess rather dull hues, but show a high degree of fastness to light and to crease-resist finishing. This also applies to reactive dyes. Their substantivity is fairly high, particularly in the case of the J-acid derivatives, hence, although they give a good yield when applied by the exhaustion method, they tend to stain white grounds in printing. The substantivity is altered only slightly by the use of nickel, but is reduced to a marked extent with 1:1, and even more with 1:2, chromium complexes (Fig. 11). Doubling the molecule causes these products to diffuse relatively slowly, so a longer time is needed to wash out unfixed dye completely. Since they contain two reactive groups per molecule, cross-linkages are formed when they react with the cellulose, thus rendering it insoluble in cuprammonium; this is not the case with ordinary monochlorotriazine dyes.

ANTHRAQUINONE DERIVATIVES

The acid anthraquinone derivatives mainly span the colour range from violet to green. They

exhibit relatively low substantivity and are therefore easy to wash off. Most of them also possess excellent fastness to light and to crease-resist finishing, but they are not dischargeable. The position of the cyanurated amino group has again a very considerable influence on the colour (Fig. 12).

PHTHALOCYANINE DERIVATIVES

Phthalocyanine polysulphonic acids are the starting products for turquoise blue dyes. They are converted into sulphochlorides which, in turn, are reacted with compounds which contain amino groups and carry the reactive groups. The remaining sulphonic groups are regenerated. Very marked differences in yield are obtained, depending on the nature of the reactive group (Fig. 13).

An intermediate compound has to be used in order to produce triazine derivatives, viz. a diamine to which both the dye and the chlorotriazine ring can be attached.

On account of their relatively large molecules, all phthalocyanine derivatives diffuse slowly and are difficult to wash off. It was with these dyes, where there are fewer possibilities of modification as regards washing-off properties, that a positive contribution from the application side was urgently needed. The newly-developed Cibacron Detergent 6892H has met this need admirably. The advent of this product provides a broader basis for the creation of new Cibacron dyes, particularly as regards batchwise exhaustion dyeing, for which dyes of higher substantivity are required. It is to be hoped that this success will pave the way for an extension of the Cibacron range.

* * *

The work done in connection with this paper was carried out under the direction of Dr. W. Widmer, and Dr. H. Riat was responsible for all the preparatory experimental work. The author expresses his thanks to these and other colleagues who rendered valuable assistance.

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(MS. received 12th May 1959)

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The Reactions of Cold-dyeing Procion Dyes with Cellulose

T. L. DAWSON, A. S. FERN, and C. PRESTON

One-day Symposium on "Reactive Dyes" held by the Manchester Section at the Manchester College of Science and Technology on 20th March 1959, Mr. J. W. Reidy in the chair

The historical development of reactive dyes for cellulose and wool is reviewed briefly. The reactions of dichloro-*s*-triazinyl dyes with water, cellulose-model compounds and with the primary and secondary hydroxyl groups of cellulose are discussed and a scheme for describing the fixation of these dyes under mild and severe conditions of alkalinity and temperature is presented. Paper chromatography, colour reactions in presence of a pyridine-caustic soda mixture, and cuprammonium solubility have helped to provide the evidence on which this scheme is based.

Historical*

The progress made from 1895 to 1957 in devising coloured compounds which can be linked to fibres by covalent bonds is summarised in Table I, in which it is clearly advantageous to include the advances made on wool, as well as on cellulose, in order to follow the thread of an idea which persisted throughout, namely that of achieving high wet fastness by a simple process.

* This brief historical review of reactive dyes was written at the request of the Manchester Section of the Society to serve as the introduction to the One-day Symposium comprising papers by Wegmann¹, Bohnert² and the present authors. The assistance of these other workers in preparing material for inclusion in the historical section is gratefully acknowledged, but the conclusions drawn are the responsibility only of Dawson, Fern, and Preston.

The starting point is Cross and Bevan's work in 1895 on a process for producing coloured esters in six stages. This is of academic interest only, since it would be quite impracticable on a works scale. In 1923 Ciba patented dyes containing the halogenotriazinyl group for fast dyeings on wool. It was probably not realised that reaction with the fibre had occurred, and it is interesting to note that one of the dyes claimed is similar to those used successfully on cellulose today. In 1925 the first dye which was *known* to react with the fibre was disclosed when Günther (BASF) patented coloured derivatives of isatoic anhydride which formed esters on heating with cellulose. The dyes were

TABLE I

Date	Discoverers	Cellulose	Discovery	Wool
1895	Cross and Bevan	Coloured esters by a six-stage process ³		—
1923	Ciba	—	Halogenotriazinyl dyes giving fast dyeings ⁴	—
1925	BASF (Günther)	Coloured derivatives of isatoic anhydride reacted with cellulose ⁵		—
1926	Peacock	Coloured ethers of low light fastness ⁶		—
1929	IG	—	Acid dyes containing the chloro-acetyl amino group giving fast dyeings ⁷	—
1930	Ciba (Haller and Heckendorn)	Soda cellulose + cyanuric chloride in xylene, treated with amines, etc. ⁸		—
1937	IG	—	Water-soluble anthraquinone dyes containing reactive halogen ⁹	—
1940	ICI	—	Work on chloroacetyl dyes commenced	—
1949	Hoechst	Evaluation of vinyl sulphone reactive system ¹⁰	Evaluation of vinyl sulphone reactive system ¹⁰	—
1952	Guthrie	Cellulose ethers from alkyl sulphate dyes, fixed by baking ¹¹		—
	Warren, Reid, and Hamalainen	Action of cyanuric chloride on cotton ¹²		—
	Hoechst	—	Remalan dyes (vinyl sulphone type)	—
1953	Ciba	—	Cibalan Brilliant dyes containing a reactive system	—
1954	ICI (Rattee and Stephen)	Investigation of dichlorotriazinyl dyes ¹³		—
1956	ICI	First dichlorotriazinyl (Procion) dyes marketed		—
1957	ICI and Ciba	First monochlorotriazinyl dyes (Procion "H" and Cibaeron) marketed		—
	Hoechst	First Remazol dyes (vinyl sulphone type) marketed		—

obviously of no commercial importance, since nothing more has been heard of them.

In 1926 Peacock recorded the first attempt to make coloured ethers (as opposed to esters) of cellulose starting from *m*-nitrobenzyltrimethylphenylammonium chloride. This work created little interest, but was followed up by Guthrie in 1952. In 1929 German workers introduced the *o*-chloroacetyl amino group into wool dyes, a contribution which was important, not in its own right, since the orange dye marketed (C.I. Acid Orange 30) was not of much commercial value, but as the starting point for two later developments of significance, viz. (a) the use of this group in commercial anthraquinonoid dyes for wool, and (b) work on the reactive systems developed by I.C.I.

A year later Ciba chemists were working on a practical dyeing process which used the reaction between cyanuric chloride and cellulose, but they could suggest only techniques based on organic solvents, which were obviously difficult to operate in bulk. Work on wool dominated the picture until 1949, of particular importance being the I.G. contribution on dyes which were proved to react under alkaline conditions by virtue of a reactive halogen atom in the anthraquinone nucleus; this was also the period in which I.C.I. commenced its work on reactive dyes for wool. It is important to note that the basic work on vinyl sulphones—the forerunners of the Remazol reactive system—was begun in 1945, culminating in the introduction of Remalan dyes for wool late in 1952. In the same year American activity (although not by dyestuff makers), became noticeable, with the work of Guthrie on cellulose ethers from alkyl sulphate dyes which were fixed by a baking treatment. Some more detailed studies of the cyanuric chloride-solvent process by Warren, Reid, and Hamalainen are noteworthy in that they undoubtedly revived research in Europe. In 1953 the Remalan dyes were joined by certain Cibalan Brilliant dyes as commercially available products containing a group capable of reaction with wool. It is doubtful whether it was realised at the time that the good wet fastness of these dyes was a result of dye-fibre reaction involving formation of a covalent linkage.

After these rather tentative beginnings, the era of reactive dyes came into full being with the introduction by I.C.I. of the Procion dyes for cellulose. The first I.C.I. patents covering the application of halogenotriazinyl reactive dyes to cellulose were dated 1954. The main contribution to this work, which had its roots in the research on wool initiated in 1940 (stimulated by the earlier German, Swiss, and American investigations), was made by Rattee and Stephen, who solved the problem of producing fast dyeings on cellulose by a simple and practical process. It would be difficult to overemphasise the magnitude of this contribution, since it triggered off intense activity, not only by I.C.I., but by the Swiss and German firms, with the result that reactive dyes are now established in markets throughout the world.

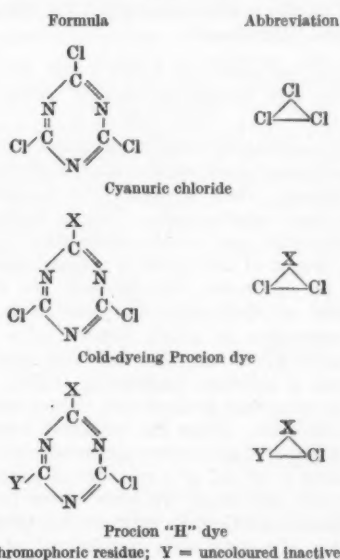
In 1956 I.C.I. introduced the first three of what was to become a wide range of dichloro-*s*-triazinyl dyes, and in 1957 commercial activity spread to

the monochloro-*s*-triazinyl system with the release of a wide range of Procion "H" and Cibacron dyes. Later that year Hoechst marketed the Remazol dyes, based on the vinyl sulphone reactive system, for application to cellulose.

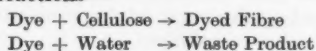
Introduction

Much practical information about the dichloro-*s*-triazinyl reactive dyes (cold-dyeing Procion dyes) is already available in pattern cards, information leaflets and scientific and trade journals. There is also a growing body of information on the mechanism by which these dyes are adsorbed and fixed¹⁴⁻²⁴. The present paper discusses some recent investigations which were designed to throw light on the reactions occurring in a system containing dichloro-*s*-triazinyl dye, water, and cellulose under known and controlled conditions. This background knowledge was required in order that the most satisfactory application processes might be devised and difficulties might be anticipated and prevented.

The behaviour of direct dyes and vat dyes can usually be explained and predicted if certain equilibrium and kinetic characteristics of the dye-cellulosic fibre system are measured. This is the classical physical chemical approach to dyeing research into systems where the forces holding dye to fibre are comparable in strength with those binding adjacent cellulose chains. Such information is insufficient for reactive dyes. Although affinity and diffusion play an important part, since they determine the proportion of dye in contact with the fibre at any moment during the dyeing operation, the rates of reaction of dye with fibre and with water are also important. Once suitable conditions are established for combination, there is no equilibrium in this type of system, and reaction ceases only when all the dye is either bonded to the cellulose or rendered inactive by hydrolysis. The substrate and the dyeing medium cannot be regarded as relatively passive components of the dyeing system, as they usually are for direct dyes



and vat dyes, but must be treated as equal partners with the dye, engaging in the simultaneous chemical reactions—



Some of the basic chemistry and abbreviated chemical formulae used in this paper are shown on p. 211. Cyanuric chloride contains three chlorine atoms, whose individual reactivity with hydroxyl or amino groups is dependent on the number of other chlorine atoms present. It has an aromatic type of resonance structure, and the chlorine atoms behave like those in aromatic acid chlorides; for example, they give pseudo-esters by reaction with the hydroxyl groups of cellulose.

Experimental

CHROMATOGRAPHIC SEPARATION OF DYE SPECIES AND REACTIVE PRODUCTS

The dye solution before and after reaction with alkali in the presence or absence of other reactants was applied to chromatographic paper (Whatman 3 MM) by means of a micropipette: 0.01 ml. of a solution containing about 40 g. dye per litre is a convenient quantity.

The chromatogram was developed in a conventional partition chromatography apparatus by downward displacement using a 4:1 Cellosolve-water mixture. After development the relative percentages of the various species present were estimated by scanning the chromatogram with an optical densitometer using appropriate filters. In order to reduce the blank correction for the optical density of the paper, the chromatogram was rendered translucent by treatment with light mineral oil, excess being removed with filter paper before taking optical density measurements.

ESTIMATION OF DYE FIXED ON THE FIBRE

Dye fixed on the fibre was estimated by dissolving portions of fabric, before and after washing off, in concentrated sulphuric acid, followed by optical measurement of the diluted extracts by the method described for vat dyes by Michie and Thornton²⁵.

ESTIMATION OF RATE OF HYDROLYSIS OF DYE BY MEANS OF THE PYRIDINE-CAUSTIC SODA COLOUR REACTION

Dichloro-s-triazinyl compounds (and most monochloro-s-triazinyl compounds) show a characteristic colour change when treated with a mixture of pyridine and caustic soda. This is indicated by a characteristic peak in the absorption spectrum, and the height of this peak is proportional to the amount of unreacted dye present. In a typical experiment to determine the rate of hydrolysis of a Procion dye in alkali, 500 ml. of a solution of dye in 0.5 N. sodium chloride were mixed with 500 ml. of a solution containing 0.2 N. alkaline buffer (to give the desired pH value) and 0.5 N. sodium chloride. After the required intervals of time, samples (10 ml.) were removed and immediately added to 85 ml. of a mixture of pyridine and caustic soda and made up with water to 100 ml. The pyridine-caustic soda mixture was prepared by mixing 5 g. of caustic soda and 550 ml. of pyridine

and diluting with water to 1 litre. After an interval of time (which varies from one dye to another) to allow the characteristic peak to develop its maximum value, the height of the peak was measured. In this way the concentration of residual dichloro-s-triazinyl dye could be determined after known times. From these results a graph of log (initial conc./conc. at time *t*) against time could be drawn. In all cases linear relationships were found, showing that the hydrolysis reaction follows first-order kinetics, the slope of the line being equal to reaction constant/2.303.

DETECTION OF REACTIVE CHLORINE ON FABRIC BY PYRIDINE-CAUSTIC SODA REACTIONS

The fabric was immersed for about 5 min. in 10% aqueous pyridine, squeezed and reimmersed in a solution containing, by vol., 12% N-NaOH, 47% pyridine, and 41% water. The change of colour was complete within 2-3 min. Since strong alkali alone gives a colour change with some dyes, it is advisable to take account of this by boiling a second sample (to remove active chlorine) in N-NaOH for 2-3 min. before treating in the above manner. The colour of this control sample can then be compared with that of the sample containing reactive chlorine. Dyes which show to advantage the characteristic colour change due to the presence of reactive chlorine are Procion Brilliant Blue R, Procion Blue 3G, and Procion Yellow R.

RATE OF REACTION OF PROCION DYES WITH HYDROXYL-CONTAINING COMPOUNDS

Since the reaction product of a Procion dye and a hydroxyl-containing compound also may exhibit a characteristic colour reaction with pyridine-caustic soda, the method described above could not be used to follow this reaction. For this purpose the rate of reaction of dye with a 50% solution of the appropriate alcohol at the desired pH value was followed by estimation of the liberated chloride ion by rapid electrometric titration of the reaction mixture with silver nitrate, after acidification with nitric acid, using a silver-silver chloride electrode.

INSOLUBILITY OF PROCION-DYED FIBRES IN CUPRAMMONIUM HYDROXIDE

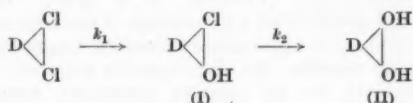
The dyed yarns were observed microscopically ($\times 50$). A cuprammonium hydroxide solution as used for viscosity measurements (15 g. copper per litre) was introduced to the yarn under a cover glass: a fibre was deemed insoluble if it remained visible as a fibre after contact for 10 min.

Results and Discussion

REACTIONS WITH WATER

The reaction of the dichloro-s-triazinyl dye with water is a feature common to all methods of application and must be considered in any fundamental study of reactive-dye fixation. Under mildly alkaline conditions in the cold, only one chlorine atom per molecule is readily lost by hydrolysis, with probable formation of a monochloromonohydroxy dye (I), where D is the chromophoric system. Wegmann²⁶ has suggested that this monochloro compound undergoes keto-enol tautomerism, in view of its abnormally low

reactivity. Under more severe hydrolysis conditions, the dihydroxy compound (II) is formed. Some dyeing, and most printing, processes are performed under conditions where both the intermediate and the final product of hydrolysis can be formed. The course of the successive hydrolysis reactions—



has been followed by means of paper chromatography (together with examination of dyeing properties and the pyridine-NaOH test) in the case of Procion Yellow R, using a dye solution containing 25 g. sodium carbonate per litre, at 60°C. The results are illustrated in Fig. 1.

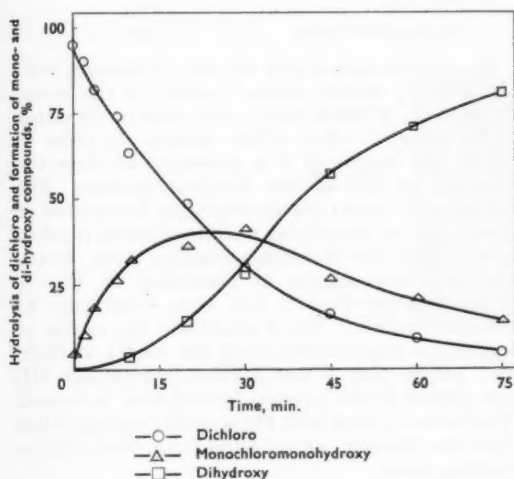


Fig. 1—Hydrolysis of Procion Yellow R (25 g. soda ash per litre at 60°C.)

Sufficient solution was used to ensure that the acid liberated by hydrolysis did not significantly affect the pH, so both reactions can be regarded as pseudo-unimolecular. The initial rise, and then fall, of the percentage of I is exactly as predicted from the assumption that the two reactions take place successively.

The rate at which dichloro-s-triazinyl dyes react with water is dependent on the dye structure, pH, and temperature. Under conditions where first-order kinetics apply (i.e. no pH change during hydrolysis), the rate constant k_1 for the formation of I is seen to be dependent on pH (Fig. 2) and on temperature (Fig. 3).

Although the dyes examined clearly behave in an individual manner as far as rate of hydrolysis is concerned, the dependence of this rate on pH or temperature is similar for all. This might be expected, as the reaction in each case involves removal of one chlorine atom from a cyanuric chloride residue.

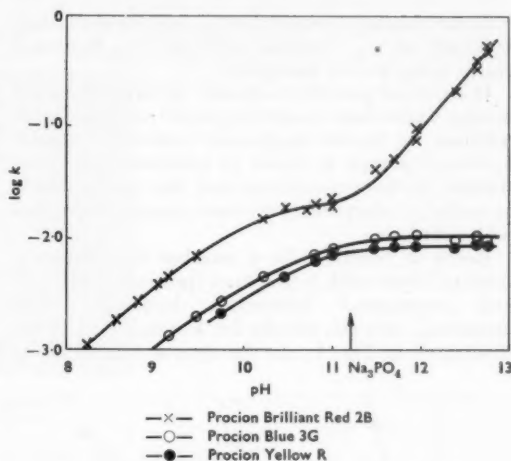


Fig. 2—Effect of pH on the Hydrolysis of Procion Dyes

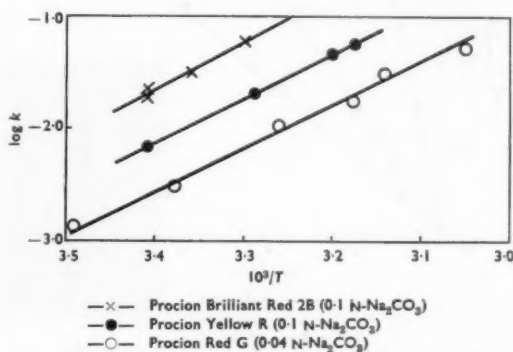
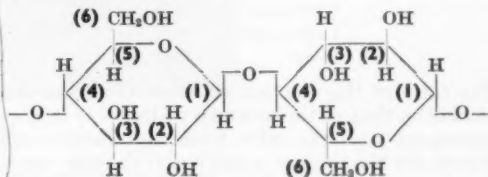


Fig. 3—Effect of Temperature on the Hydrolysis of Procion Dyes

REACTIONS WITH MODEL COMPOUNDS

Although cellulose contains hydroxyl groups, and might be expected to react with dichloro-s-triazinyl dyes in the same manner as water, the position must be complicated, not only by the insolubility of cellulose in water (which leads to a heterogeneous dyeing system), but also by the difference in character between the hydroxyl groups of cellulose and water. The hydroxyl groups of cellulose are chemically similar to those of aliphatic alcohols; they are primary ($-\text{CH}_2\text{OH}$) or secondary ($=\text{CHOH}$) and are of different degrees of reactivity in presence of an esterifying agent. Thus Gardner and Purves²⁷ have shown that toluene-*p*-sulphonyl chloride reacts with the three hydroxyl groups at $\text{C}_{(6)}$, $\text{C}_{(2)}$, and $\text{C}_{(3)}$ in the ratio—23.4:2.16:0.106.



If dichloro-s-triazinyl dyes behave as esterifying agents, therefore, they will probably react with

both the primary hydroxyl at C₍₆₎ and the secondary hydroxyl at C₍₂₎, reaction with the C₍₃₎ hydroxyl group being almost negligible.

It is not yet possible to detect, by direct chemical means, where these reactive dyes are combined with cellulose, so model compounds containing similar hydroxyl groups to those in cellulose were next studied, in the expectation that the results would be useful in interpreting the more complex reactions with cellulose.

Rates of reaction for a number of dichloro-s-triazinyl dyes with *n*-propanol (primary hydroxyl) and isopropanol (secondary hydroxyl) were measured, and the results for Procion Red G are illustrated in Fig. 4. As the dyes are insoluble in

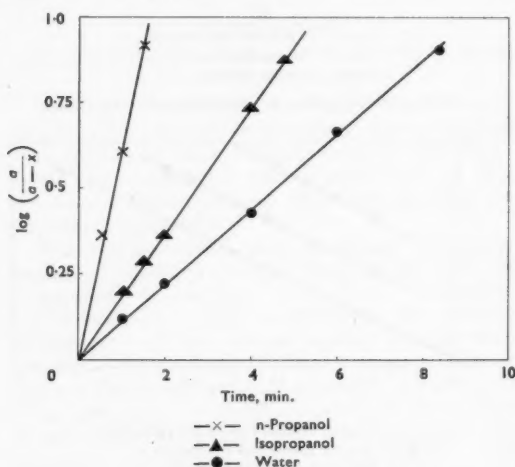
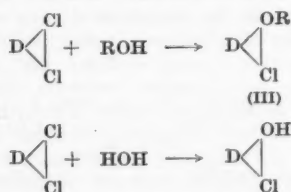


Fig. 4—Reaction of Procion Red G with *n*-Propanol and Isopropanol

the pure alcohol it was necessary to measure the rates in 50% aqueous alcohol and correct for the rate in water alone by carrying out a control experiment, on the assumption that the reactions—



(where R is the aliphatic residue) proceeded independently.

The reaction constants were found to be—

	<i>k</i> (min. ⁻¹)
<i>n</i> -Propanol	0.58
Isopropanol	0.08
Water	0.12

The ratio of the reaction constant of the normal alcohol to that of the secondary alcohol is in good agreement with the ratio found by Gardner and Purves for the toluene-*p*-sulphonyl chloride esterification at the C₍₆₎ and C₍₂₎ positions in cellulose. This ratio is of a similar order for many other Procion dyes, and it is reasonable to assume that

reaction with both types of hydroxyl group can take place in cellulose, although the rate with the primary group will be many times faster than that with the secondary hydroxyl. The relative rates of reaction with the primary and secondary propanols are given in Table II for a number of dyes, including two of the less reactive monochloro-s-triazinyl (Procion "H") type. These results, together with a knowledge of the behaviour of these dyes in application processes, suggest that the more reactive the dye towards cellulose, the greater will be its relative reactivity towards secondary hydroxyl groups.

TABLE II

Procion Dye	Ratio of Rates (primary/secondary)
Brilliant Red 2B	3.7
Red G	5.9
Brilliant Blue R	6.6
Yellow R	7.2
Blue HB	13.4
Brilliant Red H3B	15.2

It could be argued that the rate of reaction with the primary alcohol-water mixture, in the model experiment, is faster than with water alone owing to the catalytic effect of the alcohol. In order to refute this argument it is necessary to show the presence of III in the reaction mixture. The technique of paper chromatography has proved of great value in identifying various coloured reaction products of the dichloro-s-triazinyl dyes, and a typical chromatogram is illustrated in Fig. 5, where Procion Red G has been hydrolysed to different extents. Fig. 6 illustrates the results of hydrolysis experiments using the model alcohols, and proves that a new species, presumably III, not present in the aqueous hydrolysate, is formed. This is less evident with the secondary alcohol than with the primary, as expected from their relative reaction rates.

The reaction rates of a number of hydroxyl-containing model compounds, compared with water, are given in Table III for Procion Red G and Brilliant Red 5B, under standard conditions of pH and temperature. These dyes react more quickly with all the organic compounds than with water; the results with glucose and α -methyl glucoside are particularly interesting, as they suggest that Procion dyes could react at least 5–7 times as rapidly with cellulose hydroxyl groups as with

TABLE III

Reaction Rates with Various Hydroxy Compounds
Relative to Water
(Procion dye in 0.1 *N*-NaOH at 20°C.)

Procion Dye	Compound	Relative Rate of Reaction
Red G	Water	1.0
	Methyl alcohol	12.3
	Ethyl alcohol	7.4
	<i>n</i> -Propanol	4.8
	Isopropanol	0.7
	Glucose	5.5
Brilliant Red 5B	α -Methyl glucoside	6.2
	Glucose	6.6
	α -Methyl glucoside	7.1

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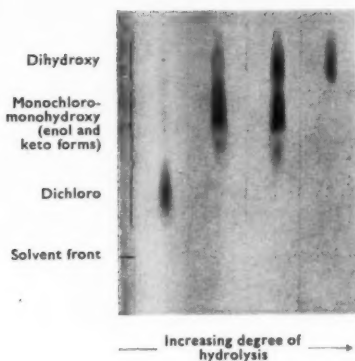


FIG. 5—Chromatographic Separations from Procion Red G

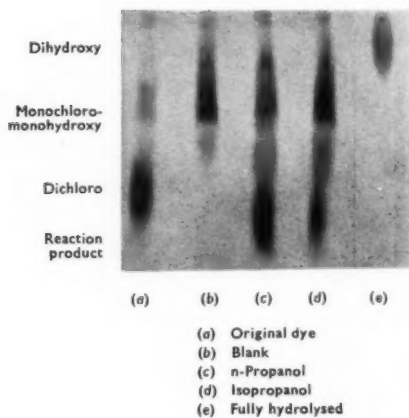


FIG. 6—Reaction of Procion Red G with Alcohols

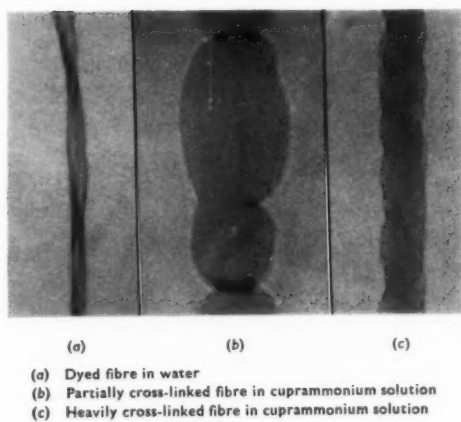


FIG. 7

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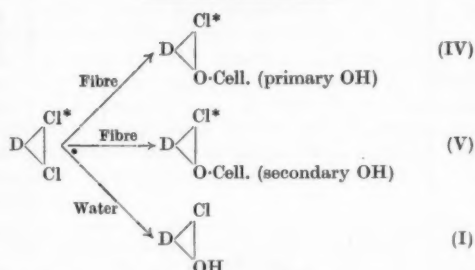
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water. This fact alone would explain the percentage fixations normally obtained from Procions in dyeing or printing, viz. about 70–90%.

REACTIONS WITH CELLULOSE

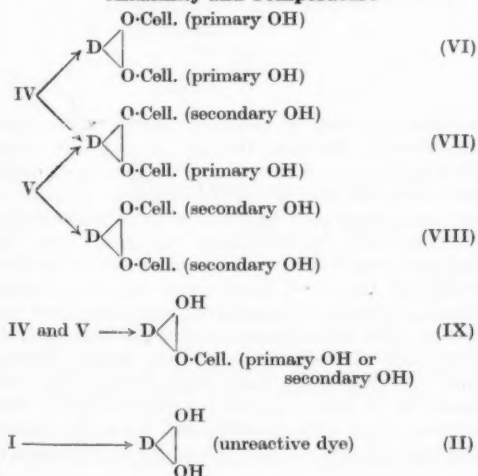
The work so far described leads to a working hypothesis that dichloro-*s*-triazinyl dyes can react with the primary, as well as with the secondary, hydroxyl groups of cellulose, the rate of reaction with the primary groups being several times that with water or with the secondary hydroxyl groups, at the same pH and temperature. Possible reactions when a dye is in contact with cellulose in presence of alkali are as follows—

Initial Reactions with Cellulose under Cold Mildly Alkaline Conditions



* Cl can be detected by pyridine-NaOH reagent.

Subsequent Reactions under Conditions of Higher Alkalinity and Temperature



Under mild conditions only one chlorine atom reacts, giving the two cellulose derivatives, IV and V, in the ratio of 3–7:1 (depending on the dye) by analogy with the rates of reaction with the model alcohols (see Table II). Consequently, between 12½% and 25% of the fixed dye may be attached to secondary hydroxyl groups.

The presence of the labile chlorine (asterisked in IV and V) can be demonstrated on the dyed fibre by its colour reaction with pyridine-NaOH.

The scheme above also indicates further reactions which may occur when the fixation conditions are made more severe: the monochloro-*s*-triazinyl forms of the dye in which a cellulose chain is one

of the substituents (IV and V) can combine with another hydroxyl group. Examination of molecular scale-models suggests that this further combination is much more likely to take place with the hydroxyl group of a second cellulose chain than with a hydroxyl group in the same anhydroglucose unit or in another unit of the same chain. Thus three cross-linked species (VI, VII, and VIII) are theoretically possible. Assuming that the ratio of the primary and secondary hydroxyl reaction rates is the same for the second chlorine atom as for the first, these cross-linked forms should be present in the following ratios—

Form of Cross-link	Primary:Secondary Reaction Rate Ratio	
	3:1	7:1
Primary-primary (VI)	9	3.5
Primary-secondary (VII)	6	1
Secondary-secondary (VIII)	1	negligible

Therefore, when any cold-dyeing Procion dye is applied under conditions where cross-linking is likely, at least two, and possibly three, different forms of cross-linked cellulose chains may be present, the proportion of primary-primary bound hydroxyl always being much greater than that of a linkage involving a secondary hydroxyl group.

Species I, IX, and II are produced by reactions of the dye with water or of the dyed fibre containing IV and V with water.

The only convincing way of proving that dichloro-*s*-triazinyl dyes are capable of cross-linking cellulose chains is to form, and identify, a hydrolysis product from the dyed cellulose consisting of, say, two glucose or cellobiose units joined by a dye molecule. This has not yet proved possible by chemical or enzymatic means, and the cross-linking reaction must, therefore, be inferred from the profound changes in fibre swelling and solubility which occur when even small amounts of dichloro-*s*-triazinyl dye are applied under conditions favourable to the reaction of both chlorine atoms. Fig. 7 illustrates the behaviour of a dyed fibre in cuprammonium hydroxide solution when the dye has been applied under conditions which give rise to (b) slight and (c) much cross-linking.

Vickerstaff²¹ has published figures showing the extremely small amounts of dye necessary to cause significant changes in the behaviour of cotton and viscose rayon when placed in a cuprammonium solution. Some of these data are reproduced in Table IV.

TABLE IV
Insolubilisation of Cellulose in Cuprammonium Hydroxide

Dye	Dye on Fibre (%)		Anhydro- glucose Units per Dye Molecule
	Soluble	Insoluble	
COTTON			
Procion Brilliant Red 2B	0.05	0.08	5,000
Procion Yellow R	0.03	0.05	7,500
Procion Blue 3G	0.06	0.09	5,000
VISCOSE RAYON			
Procion Blue 3G	0.4	0.7	600

According to current theory, the solubility of cellulose in cuprammonium solution arises from the rupture of interchain hydrogen bonds by the powerful co-ordination action of the solvent on the hydroxyl groups at $C_{(2)}$ and $C_{(3)}$, which must be in a *cis*- or strained *cis*-relationship to one another²⁸. The length of the cellulose chains and the crystallinity of the fibre must also play an important part in determining the rate of solution. If the chains in cotton are about 3,000 anhydroglucose units long²⁹, it is evident that, on average, one dye molecule is sufficient to join two cellulose chains, thus doubling the mol. wt. of the chain and converting a soluble compound into an insoluble one. With viscose rayon, on the other hand, the chain length has only about 600 anhydroglucose units, so 10 chains must be linked before the mol. wt. reaches the level at which insolubility occurs in the case of cotton. This requires 9 dye molecules, a figure which is surprisingly close to that predicted from the relative amounts of Procion Blue 3G required to insolubilise cotton and viscose rayon (Table IV). This must be an over-simplification, because the dye is not uniformly distributed, particularly in the case of viscose rayon, owing to ring-dyeing (according to Vickerstaff), and no allowance can be made for the "wastage" of dye which occurs if two chains are joined by more than one dye molecule. These two errors, however, tend to cancel one another.

The course of the cross-linking reaction can be followed in the case of Procion Brilliant Red 2B by using increasing concentrations at various pH values, so that the region in which sufficient dye is present to insolubilise the fibre is determined as a function of pH. A large number of experiments would be needed to determine precisely the point at which insolubilisation occurs, so the simpler expedient was adopted of choosing two concentrations of dye, one representing a soluble and the other an insoluble fibre, and determining the concentration range in which insolubilisation occurs. From Fig. 8 it is seen that the amount of dye needed for insolubilisation falls to a minimum at about pH 11.2 and then increases again. This suggests that the proportion of dye present in the cross-linked form at first increases as the dyebath alkalinity is raised, but that at higher pH values at least one of the bonds joining cross-linked dye to the cellulose is broken by alkaline hydrolysis to give a compound of type IX.

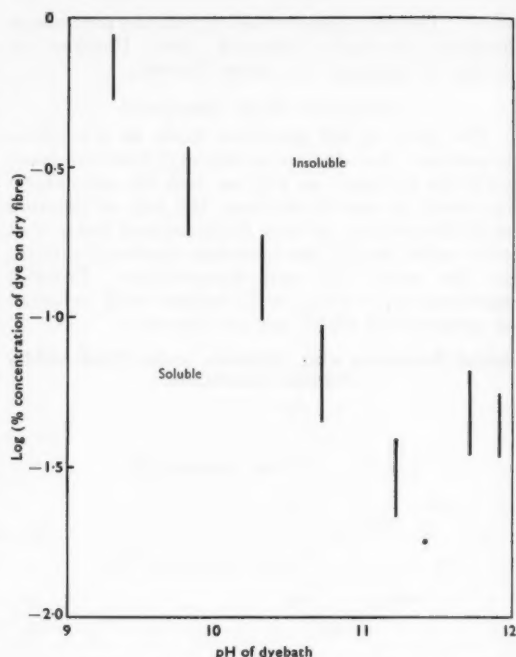
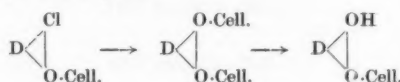


Fig. 8—Effect of pH in Producing Insolubility in Cuprammonium Hydroxide (Procion Brilliant Red 2B on Cotton)

Finally, the sequence—



was demonstrated by treating viscose rayon, dyed with Procion Brilliant Orange G, in alkali under different degrees of severity. The fibre dyed under mild conditions (IV and V) was soluble in cuprammonium, but with a relatively mild alkaline aftertreatment cross-linking occurred and the fibre was insolubilised. Under more severe alkaline conditions the dyed fibre again became soluble. Parallel behaviour was shown when the fibre was treated with concentrated sulphuric acid, a technique used by Schwertassek¹⁹ to study Procion dyes. As the fibre was cross-linked, the concentration of acid required for dissolving the fibre increased from 50% to 80%, but fell to 50% again after the second, more severe alkaline treatment of

TABLE V
Reactions of Viscose Rayon with Procion Dyes

Reactants	Conditions	Product	Behaviour in Cuprammonium	Behaviour in Sulphuric Acid
$\begin{array}{c} \text{Cl} \\ \diagup \quad \diagdown \\ \text{D} \triangle \quad \text{O-Cell.} \end{array} + \text{Cellulose}$	Cold pH 8 72 hr.	$\begin{array}{c} \text{Cl} \\ \diagup \quad \diagdown \\ \text{D} \triangle \quad \text{O-Cell.} \end{array}$	Soluble	Soluble in 50% acid; insoluble in 47.5% acid
$\begin{array}{c} \text{Cl} \\ \diagup \quad \diagdown \\ \text{D} \triangle \quad \text{O-Cell.} \end{array} + \text{Cellulose}$	Cold pH 11 (Na_2CO_3) 24 hr.	$\begin{array}{c} \text{O-Cell.} \\ \diagup \quad \diagdown \\ \text{D} \triangle \quad \text{O-Cell.} \end{array}$	Insoluble	Soluble in 80% acid; insoluble in 77.5% acid
$\begin{array}{c} \text{O-Cell.} \\ \diagup \quad \diagdown \\ \text{D} \triangle \quad \text{O-Cell.} \end{array}$	Hot (100°C.) pH 11 (Na_2CO_3) 30 min.	$\begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{D} \triangle \quad \text{O-Cell.} \end{array}$	Soluble	Soluble in 50% acid; insoluble in 47.5% acid

the dyed fibre. The results are summarised in Table V.

Conclusion

In this paper is described some of the work in progress on the mechanism of reactive-dye fixation—work which is complementary to the development of application processes at a more practical level. A great deal of information is still lacking, and it is impossible to state categorically how and where reactive dyes are fixed. Their general behaviour under various conditions of pH, time, and temperature can, however, be predicted from information such as that given here. There is another aspect to this work, since in order to solve many of the problems more knowledge about cellulose itself is required. Specifically, very little is known about the absorption of alkalis by cellulose, and clearly this must play an important part in reactive-dye fixation. It is hoped by pursuing this fundamental work, not only to help users of Procion dyes to understand the reactions which they bring about, but to gain information of value in other fields of preparation, dyeing, and finishing where aqueous alkalis are in contact with cellulose.

* * *

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COMMUNICATIONS

The Dyeing of Cellulose Acetate with Disperse Dyes IX—Effect of Varying Acetyl Value

C. L. BIRD and G. TABBRON

Fibre saturation values have been determined at 90°C. for two groups of three similar disperse dyes on secondary cellulose acetate, cellulose triacetate and three cellulose acetates of intermediate acetyl value. The results have been correlated with the accessibility of the substrates and the hydrophobic character of the dyes and substrates. The rates of dyeing at 90°C. of two commercial dyes on the five yarns were found to decrease with increasing acetyl value, especially above 58% acetic acid content.

INTRODUCTION

Cellulose triacetate was first marketed in fibre form in this country in 1954, under the names *Tricel* (BrC) and *Courpleta* (Courtaulds). Compared with the secondary acetate fibre (54–55% acetic acid content), available since 1921, triacetate rayon swells much less in water and therefore dyes more slowly. It is more crystalline than secondary acetate and should therefore show lower fibre saturation values for dyes. The physical and dyeing properties of triacetate rayon have been described by Boulton¹ and by Mellor and Olpin².

The dyeing properties of cellulose acetate are evidently related to its acetyl value, so it was decided to measure the rate of dyeing and maximum uptake of disperse dyes on cellulose acetate yarns within the range 54.0–62.1% combined

acetic acid. During the course of this investigation a paper describing similar work was published by Fortess and Salvin³, who say—“We have not found any commercial disperse dye which dyes the triacetate fibre more rapidly and to a greater extent than it does the secondary acetate fibre under identical conditions”. They found that rate of dyeing is constant between 52% and 58%, and relatively slow above 60%, acetic acid content (cf. Fig. 6). Experiments with three azo dyes of similar chemical constitution, but containing 0, 1, and 2 *N*-β-hydroxyethyl groups respectively, suggested a relationship between the hydrophobic nature of the dye and the fibre.

The present paper confirms these results and provides additional data.

EXPERIMENTAL

Yarns and Films

Some physical properties of the yarns and films are given in Table I.

TABLE I

Sample No.	Acetic Acid Content (%)	Regain (%)	Water Imbibition (%)
1	54.0	7.07	25.8
2	58.53	5.96	22.5
3	60.14	4.51	17.6
4	61.6	4.05	15.4
5	62.1	3.90	15.0
6	54.0	7.10	—
7	61.5	4.74	—
Film from 1	54.0	6.78	—
Film from 5	62.1	3.57	—

Yarns 1–5 (Courtaulds Ltd.) were of 140 denier, and had 32 filaments (except No. 1, which had 28 filaments), with a twist of 1 t.p.in. No. 6 was 140/26, 10 t.p.in. Celanese and No. 7 was 200/45, 0.6 t.p.in. Courpleta. After reeling into hanks (1 g., 0.5 g., and 0.2 g.), the yarn was desized by extraction with ligroin (b.p. 40–60°C.) for 24 hr. in a Soxhlet, dried below 60°C. and washed in running water for 24 hr. After rinsing in distilled water and squeezing, the yarn was conditioned in a humidity room at 65% R.H. and 22°C. Regains in Table I refer to these conditioned yarns. Water imbibitions were determined by centrifuging wet yarn for 5 min. at 1000 g in a M.S.E. Magnum centrifuge.

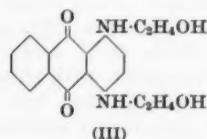
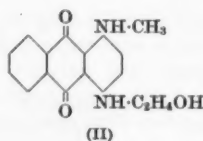
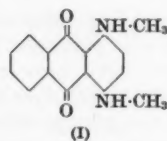
Films were prepared from yarns No. 1 and 5, as described in Part IV⁴, but in place of acetone a 60:40 methylene chloride–ethanol mixture was used.

Dyes

Purified dyes were prepared as described in Part I⁵.

Desorption

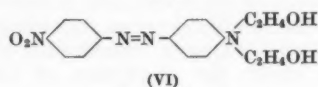
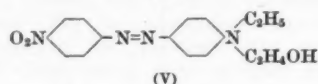
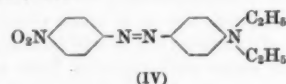
A Gilbert U-tube⁶ connected to a Lemin revolving tap⁷ was used, as described in Part VI⁸. Desorption experiments were carried out at 90°C. with a series of three blue anthraquinonoid disperse dyes, viz.—



Aqueous Solubility at 90°C. (mg./litre) ...	(I)	(II)	(III)
	4.2	55.0	103.5

With I, surface adsorption occurred during the initial dyeings (carried out as before⁸), so a preliminary 30-min. desorption was given to remove superficial dye.

A further series of red azo dyes was used to a lesser extent, viz.—



	(IV)	(V)	(VI)
Aqueous Solubility at 90°C. (mg./litre) ...	—	15.0	38.5

With IV the aqueous solubility is too low for desorption experiments to be feasible, but the fibre saturation values were determined for yarns 1 and 5 and the two films by dyeing with an excess of dye in the form of a fine dispersion in 0.002 M. sodium 1-oleyl-4-anisidine-2-sulphonate.

Desorption experiments with 4-aminoazobenzene were also included, in order to provide a comparison with the work of Majury⁹.

Rate of Dyeing

Since the rate of dyeing with disperse dyes is dependent on particle size, it was necessary to use unpurified commercial dyes in order to ensure that the particle size did not vary. Dyes I and II were used, in the form of Duranol Brilliant Blue G 300 (ICI) and Serisol Brilliant Blue 2B (YDC) respectively. Dyeings were carried out at 90°C. on 1 g. hanks for various times, in a Marney dyeing machine as before¹⁰, in presence of 1 g. Lissapol LS paste (ICI) per litre. The amount of commercial dye used was equivalent to 3.6 mg. of pure dye per 80 ml.; it was the same as that used in previous work¹⁰, and corresponds to a 1.5% dyeing of Dispersol Fast Scarlet B 150 (ICI) (V). A temperature of 90°C. was chosen for these dyeings and the desorption experiments (although previous work in this series has been carried out at 80°C.) since the adsorption and desorption of disperse dyes by cellulose triacetate at 80°C. is extremely slow.

DISCUSSION

Fibre Saturation Values

The partition coefficients for yarns 1–5, determined by desorption, have been multiplied by the aqueous solubilities at 90°C. to convert them to fibre saturation values. The results are illustrated in Fig. 1 and 2 as plots against acetyl value and regain respectively.

In Table II are given fibre saturation values for the six dyes on secondary acetate (sample 1) and triacetate (sample 5).

The lower regain of cellulose triacetate, compared with that of secondary cellulose acetate, can be

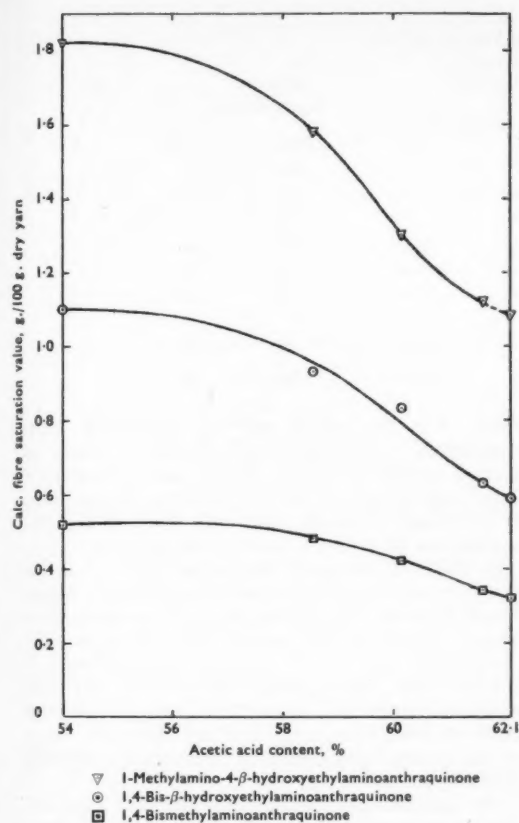


Fig. 1—Effect of Acetic Acid Content on the Fibre Saturation Value

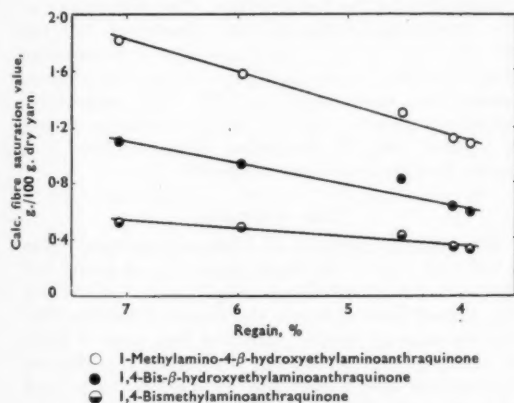


Fig. 2—Relation between Regain and Fibre Saturation Value

attributed to two factors, viz. (a) the more crystalline nature of the triacetate, resulting in lower accessibility, and (b) the very small number of water-attracting hydroxyl groups in the triacetate. Beever and Valentine¹¹ estimate that the accessibility of secondary acetate yarn varies between 0.83 and 0.95. Triacetate yarns have a somewhat lower accessibility, the figure for yarn of the type used in this work being 0.75. Although the results of Beever and Valentine cannot be applied

directly to the present work, a comparison for the two sets of figures for regain and acetyl value indicates a difference of accessibility of about 20% between the secondary acetate and triacetate used in this work. This will affect the saturation values of all disperse dyes, tending to make them lower on triacetate than on secondary acetate. In fact, the decrease in accessibility will probably be greater with the large dye molecules than with the small water molecules.

Valentine¹² estimates that, at 65% R.H., a hydroxyl group can absorb 0.5 mol. of water, whereas an acetyl group can absorb at most 0.25 mol. of water. These water molecules are presumably linked to the fibre through hydrogen bonds.

The nature of the linkage between disperse dyes and cellulose acetate is still a matter of controversy. Bird¹³ has suggested that the more hydrophilic disperse dyes, i.e. those containing *N*-β-hydroxyethyl groups, combine largely through hydrogen bonds, whereas the more hydrophobic dyes, e.g. IV, are adsorbed mainly through non-polar van der Waals forces. On this basis the most hydrophilic disperse dyes should show the greatest fall in fibre saturation value in passing from secondary acetate to triacetate. Table II shows that this is in fact the case.

Dye IV contains no hydrogen-donating group and, judged from its exceptionally high solubility in benzene¹³ and exceptionally low solubility in water⁵, is much the most hydrophobic of the dyes examined. With this dye the lower accessibility of the triacetate is outweighed by its more hydrophobic character and the net result is a greater fibre saturation value on triacetate than on secondary acetate. This dye, which is not used commercially, is, however, an exceptional case. Similar results were obtained by Fortes and Salvin³ for the corresponding *NN*-dimethyl compound. Their dyeings were not taken to equilibrium, but gave a clear indication that the fibre saturation value would be higher on triacetate than on secondary acetate.

Dye I is less hydrophobic and has hydrogen-donating groups, although these may be bonded internally with the carbonyl oxygen atoms.

At the commencement of this work it was anticipated that the two most hydrophilic dyes examined, viz. VI and (especially) III, would show very low fibre saturation values on cellulose triacetate in view of their low solubility in anhydrous ethyl acetate¹³. However, consideration of the regains for the secondary acetate and triacetate, viz. 7.07% and 3.90%, shows that the triacetate cannot be regarded as a solid anhydrous solvent, although it is more hydrophobic than the secondary acetate.

The two dyes containing one *N*-β-hydroxyethyl group are intermediate between those containing two of these groups and those containing none. With V the ratio of 81% suggests that, if the two fibres were equally accessible, the fibre saturation value would be slightly higher on triacetate than on secondary acetate.

TABLE II
 Calculated Saturation Values at 90°C.

Dye	(g./100 g. dry substrate)				$\frac{\text{Triacetate}}{\text{Sec. Acetate}} \times 100$	
	Secondary Acetate		Triacetate			
	(Sample 1)		(Sample 5)		Fibre	Film
	Fibre	Film	Fibre	Film		
I	0.52	—	0.32	—	61	—
II	1.82	—	1.08	—	59	—
III	1.10	—	0.59	—	54	—
IV	0.29	0.25	0.52	0.37	179	148
V	2.49	1.80	2.01	1.35	81	75
VI	1.13	0.88	0.71	0.55	63	62.5
4-Aminoazo- benzene	17.2	15.0	16.3	14.0	95	93
Regain (%)	7.07	6.78	3.90	3.57	55	53

The regain figures in Table II indicate that conversion of the fibres into films has resulted in some crystallisation of both acetates. The resulting lower accessibilities account for the lower saturation values on the films, as well as the lower regains.

The results for 4-aminoazobenzene at 90°C. are similar to those obtained by Majury⁹ at 80°C., but the acetyl values of his films (53% and 60.5%) were appreciably lower than those of the films used in this work (54.0% and 62.1%). Although 4-aminoazobenzene has greater aqueous solubility than any of the other dyes used, it also has good solubility in benzene (and to a less extent in hexane) and so is presumably capable of adsorption through non-polar van der Waals forces. The triacetate/secondary acetate ratio of 93–95% indicates that, with completely accessible material, the fibre saturation value would be greater on triacetate than on secondary acetate. It is noteworthy that, with the hydrophobic compound, *NN*-dimethyl-4-aminoazobenzene, Majury's figures give a triacetate/secondary acetate ratio of 126%.

4-Aminoazobenzene has also been used by Kanga¹⁴, who found that, at low to moderate crystallinities, the equilibrium absorption by cellulose triacetate falls rapidly with increasing crystallinity, further increase in crystallinity then having no effect on dye absorption.

The question arises as to whether, at a given temperature, the solubility of a dye in secondary acetate (or triacetate), i.e. its fibre saturation value, can be regarded, like its aqueous solubility, as an absolute value. Fig. 1 indicates that, with secondary acetate, small variations in acetic acid content will have little effect on the fibre saturation

value, but the effect will be noticeable with triacetates. Variation in accessibility is likely to exert a greater influence. Beever and Valentine¹¹ found a range of 0.83 to 0.95 for the accessibilities of secondary acetates, and 0.75 to 0.85 for triacetates of 61.5–62.2% acetic acid content.

In Table III are given fibre saturation values for five dyes on two different secondary acetate fibres. Apart from 4-aminoazobenzene, all the dyes show higher values on the second fibre of each pair, presumably due to its greater accessibility. It follows that fibre saturation values are not absolute values, and that the results of different workers using the same dye are likely to vary, owing to small differences in accessibility between similar yarns.

Our general conclusion is that disperse dyes will show a lower fibre saturation value on triacetate than on secondary acetate, because of the lower accessibility of the former fibre. The differences in the hydrophilic/hydrophobic character of the two fibres is not sufficiently great to influence the fibre saturation value to a large extent, apart from exceptional cases such as IV. The triacetate/secondary acetate ratio for fibre saturation values is highest with hydrophobic disperse dyes and lowest for the more hydrophilic dyes.

Rate of Dyeing

The rates of dyeing of Duranol Brilliant Blue G 300 and Serisol Brilliant Blue 2B, on yarns 1–5 at 90°C., are illustrated in Fig. 3 and 4, in which the broken lines indicate the times of half-dyeing. For the sake of clarity, only the first part of most of the curves is shown, but the equilibrium exhaustions are illustrated in Fig. 5, as a plot against acetic acid content.

Fig. 6 illustrates the effect of acetyl value on the time of half-dyeing and Fig. 7 the effect of varying water imbibition (a plot of $\log t_{1/2}$ against percentage water imbibition shows an approximately linear relation).

The curves for equilibrium exhaustion in Fig. 5 have a similar shape to those for fibre saturation value in Fig. 1, but the curves for time of half-dyeing (Fig. 6) show a steep rise above an acetic acid content of about 58%, as observed by Fortess and Salvin³. Fig. 7 supports the generally accepted view that the major factor responsible for the slow

 TABLE III
 Saturation Values at 90°C. on Different Yarns

Dye	Secondary Acetate		Triacetate	
	Sample 1	Sample 6	Sample 5	Sample 7
	(54.0% a.a.c.*)	(54.0% a.a.c.*)	(62.1% a.a.c.*)	(61.5% a.a.c.*)
I	0.52	0.54	0.32	0.38
II	1.82	2.35	1.08	1.17
III	1.10	1.36	0.59	0.72
VI	1.13	1.36	0.71	0.96
4-Aminoazo- benzene	17.2	16.7	16.3	15.7

* Acetic acid content \equiv acetyl value.

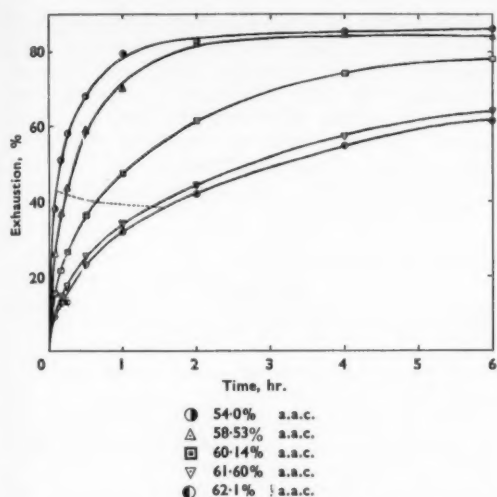


Fig. 3—Rate of Dyeing at 90°C. of Duranol Brilliant Blue G 300

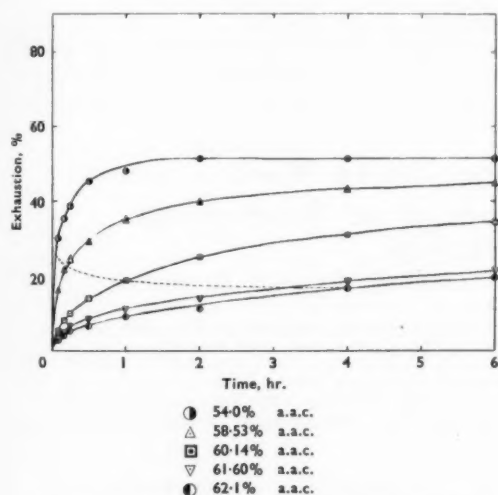


FIG. 4—Rate of Dyeing at 90°C. of Serisol Brilliant Blue 2B

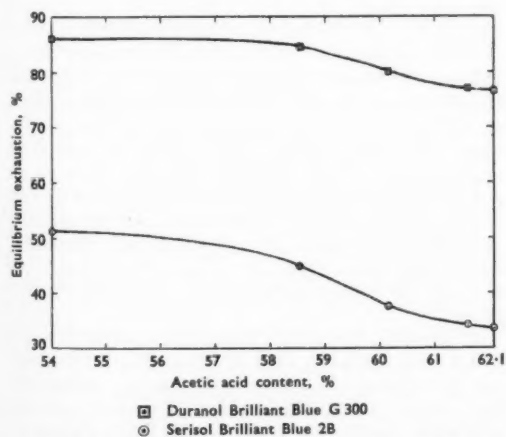


Fig. 5—Effect of Acetic Acid Content on the Equilibrium Exhaustion

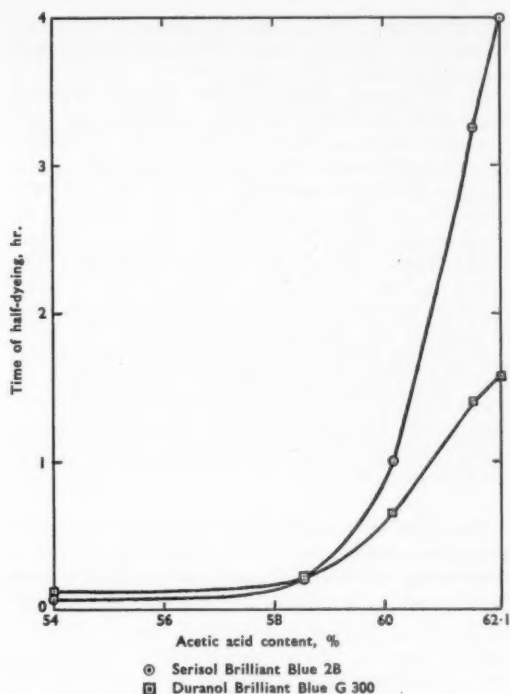


Fig. 6—Effect of Acetic Acid Content on the Time of Half-dyeing

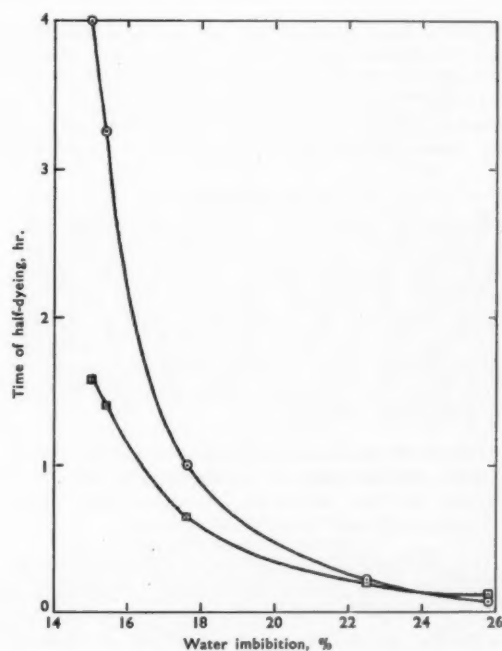


Fig. 7—Effect of Swelling on Time of Half-dyeing

rate of dyeing of cellulose triacetate is the small extent of swelling in water, indicated by the low percentage water imbibition.

On secondary acetate rayon, Serisol Brilliant Blue 2B is found to be more rapid-dyeing than Duranol Brilliant Blue G 300, a result which agrees with values for rate of diffusion of the purified dyes into secondary acetate film at 80°C. obtained by Bird, Manchester, and Scott⁴. On cellulose triacetate, however, the order is reversed; the hydrophilic Serisol Brilliant Blue 2B dyes very slowly on the hydrophobic fibre. There is some evidence that the more hydrophilic disperse dyes in general are not very suitable for the more hydrophobic fibres such as cellulose triacetate and Terylene. For example, Serisol Brilliant Blue 2B is not recommended for dyeing cellulose triacetate, presumably because of its very slow rate of dyeing and its low affinity, which together result in a poor "building-up" property.

* * *

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The Effect of Sulphuric Acid on Wool

IV—Some Further Observations of the Reaction with Concentrated Acid

R. L. ELLIOTT, R. S. ASQUITH, M. E. P. HOPPER, and D. H. RAWSON

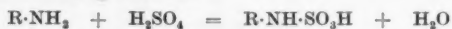
The following types of wool have been treated with concentrated sulphuric acid—virgin wool, dinitrophenylated wool, and deaminated wool. Subsequent analyses of the treated wools have shown clearly that the amino groups do not give covalent sulphamic acid derivatives, but that the aliphatic hydroxyl groups react rapidly to give sulphate esters. Serine and threonine analyses of treated wools after reaction with sulphuric acid support the theory that an *O*-peptidyl rearrangement occurs. The mechanism proposed for this rearrangement has been modified, and it is suggested that it proceeds through the aliphatic sulphate ester grouping primarily introduced into the wool.

Introduction

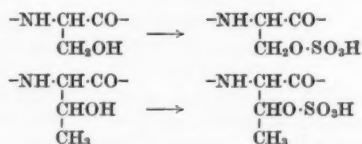
Numerous workers¹⁻³ have shown that wool treated with concentrated acid (80–98% sulphuric acid) for specific times, contains a certain percentage of sulphate radical which is only very slowly removed by continued washing. It has also been shown that the amount of sulphate bound in this manner reaches a maximum after a short time of treatment⁴, and then slowly falls off on prolonged reaction.

Two basic mechanisms have been postulated to explain the difficulty of removing sulphate, each relying on the formation of a covalent bond between wool and the sulphate radical.

(1) Harris and co-workers² suggested that the formation of sulphamic acids occurs according to the following reaction—



(2) Reitz and co-workers³ suggested that *O*-sulphate esters of serine and threonine may be formed as follows—



Each of these reactions would lead to the introduction of acidic groups, which could explain the failure of badly carbonised wool to dye levelly. Speakman and Gaafer⁵ have pointed out that sulphonation of the benzene nucleus of tyrosine and phenylalanine could occur; but sulphur bound in this reaction could not be recovered as sulphate on hydrolysis of the wool and could not, therefore, affect the percentage of recoverable sulphate (termed "hydrolysable sulphate" throughout this paper).

In previous papers^{4,6}, the present authors have shown unequivocally that sulphonation of tyrosine and phenylalanine can occur on treating either the free amino acids⁶ or wool⁴ with concentrated sulphuric acid, but, as would be expected, sulphonation is slower than the rapid uptake of

sulphate. It was also shown, by electrophoresis, that serine and threonine, on treatment with sulphuric acid, give an equilibrium mixture of the free amino acid and a sulphate ester. As these esters are hydrolysable under normal hydrolytic conditions, they could not be isolated from wool hydrolysates. However, on the basis of the maximum value obtained for hydrolysable sulphate (10.65%)⁴, it was suggested that the theory of Reitz is most probably correct.

Calculations showed that the maximum hydrolysable sulphate obtainable if all the free amino side-chains of lysine were sulphated, would be 7.60%, whereas if all the hydroxyl groups were to react, the maximum value would be 12.2%.

It has further been shown⁷ that, in an equilibrium mixture of serine and serine sulphate, as obtained by the treatment of the amino acid with concentrated sulphuric acid, the mixture consists of 90.2% serine sulphate and 9.8% serine. Assuming that the equilibrium with wool is similar, this would help to explain the fact that the actual values are lower than the calculated values.

The present work was undertaken in order to determine the precise reaction leading to the binding of sulphate radicals by the wool, i.e. to distinguish between sulphonation of amino groups and sulphonation of hydroxy groups.

Experimental

PREPARATION OF WOOL SAMPLES

(1) Raw Wool

Tips and root ends were removed from 64s Merino wool which was then degreased in a Soxhlet with ether (24 hr.) followed by alcohol (24 hr.) Burr material was removed by hand and the wool was washed with running water for 4 hr., allowed to stand in water for a further 20 hr., rinsed with distilled water, and dried in an air oven at 40°C. for 12 hr. Samples for treatment were dried overnight at 90°C. and stored over P_2O_5 in a vacuum desiccator.

(2) Dinitrophenylated Wool

A sample of dried wool (1.5 g.) was treated with a mixture of sodium bicarbonate (1.5 g.), water (30 ml.), ethanol (120 ml.) and 1-fluoro-2,4-dinitrobenzene (1.5 ml.) for 3 days at 30°C. The wool was filtered off, washed successively with ethanol, diethyl ether, dilute acetic acid, and distilled water, dried overnight in an air oven at 90°C. and stored over P_2O_5 .

(3) Deaminated Wool⁸

A sample of dried wool (5 g.) was treated with a solution of sodium nitrite (165 ml.; 255.6 g./litre) and glacial acetic acid (35.3 ml.) for 12 days at 22.2°C. in a flask fitted with an outlet valve to prevent the entry of air. The wool was filtered off, washed with running water for 4 hr., rinsed with distilled water, dried overnight in an air oven at 90°C. and stored over P_2O_5 .

TREATMENT OF SAMPLES

Samples of wool (2 g.), prepared by methods (1), (2) and (3), were separately treated with

concentrated sulphuric acid (100 ml.) for the appropriate time. The wool was then filtered off and washed successively with ether (100 ml.), acetone (100 ml.), and running water for 2 hr. The samples were rinsed with distilled water, dried overnight in an air oven at 90°C. and stored over P_2O_5 . The wool samples obtained were used for sulphate, serine, and threonine analyses.

(a) Sulphate Analyses

Wool samples (0.5 g.) were hydrolysed with 6 N. hydrochloric acid (20 ml.) for 4 hr. The solution was filtered through a small Whatman No. 1 filter paper which was washed well with water. The solution was made up to volume. Aliquots (10 ml.) were withdrawn, diluted to 100 ml., boiled, and the sulphate precipitated with 10% barium chloride solution (7 ml.). The solutions were filtered through tared No. 4 sintered-glass crucibles which were dried at 120°C. for 4 hr. and reweighed.

(b) Serine and Threonine Analyses

Serine and threonine analyses were performed simultaneously by the method of periodate oxidation⁹.

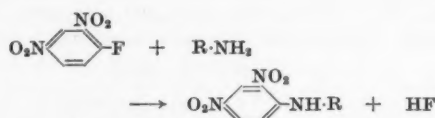
Wool samples (0.5 g.) were hydrolysed for 4 hr. with 6 N. hydrochloric acid (20 ml.). The hydrolysates were evaporated to dryness under reduced pressure below 40°C. Water (2 ml.) was added and the solution again evaporated under reduced pressure. This was repeated three times. Distilled water (25 ml.) was added to the residue, and the resulting solution was filtered through a small, Whatman No. 41 filter paper and made up to volume.

An aliquot of this solution (5 ml.) was oxidised with a mixture of 0.5 M. periodic acid (1 ml.), potassium arsenite solution (1.5 ml.), 1 N. sulphuric acid (0.3 ml.) and pH 7.6 phosphate buffer (6 ml.). Air was bubbled through the solution when oxidation of serine to formaldehyde and of threonine to acetaldehyde had occurred. The acetaldehyde was carried over in the air stream and collected in 2.5% sodium bisulphite solution. The bisulphite was titrated with 0.1 N. iodine, using a starch indicator, until the end-point was reached. The acetaldehyde was liberated from its bisulphite compound with M-sodium bicarbonate, and the liberated bisulphite was titrated with 0.01 N. iodine. The formaldehyde produced remained in the oxidation vessel, and was steam distilled and collected in bisulphite solution. The formaldehyde was then estimated by a method similar to that used for acetaldehyde. No correction was made in all cases for loss of the amino acids during hydrolysis.

Results and Discussion

If sulphonation of the amino groups is occurring at all in wool treated with sulphuric acid, it follows that any treatment which makes these groups inaccessible to this reagent will bring about a reduction in the maximum hydrolysable sulphate which is immediately taken up by the wool. A typical treatment known to have no side-reactions

is the reaction with 1-fluoro-2,4-dinitrobenzene. As is seen from the following reaction scheme, 1-fluoro-2,4-dinitrobenzene introduces a bulky side-chain, thus making the amino groups inaccessible to further attack.



When this reaction is carried out, it is seen from Tables I and II that the change in hydrolysable sulphate content, as compared with that of virgin wool, is negligible after a short treatment time with concentrated sulphuric acid. Thus virgin wool, after treatment for 10 min., has absorbed 10.65% hydrolysable sulphate, whereas dinitrophenylated (DNP) wool has absorbed 10.80%. This indicates that the amount of hydrolysable sulphate is not influenced to any degree by protection of the amino groups.

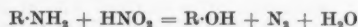
TABLE I
Analyses of Virgin Wool

Time of Acid Treatment	SO ₄ (%)	Serine (%)	Threonine (%)
10 min.	10.65	8.25	6.40
1 hr.	10.30	—	—
2 hr.	9.10	—	—
3 hr.	8.25	6.70	5.15
1 day	5.30	6.14	4.51
2 days	4.50	5.99	4.66
4 days	4.43	—	4.84
7 days	4.27	—	—

TABLE II
Sulphate Content of Dinitrophenylated Wool

Time of Acid Treatment	SO ₄ (%)
10 min.	10.80
1 hr.	9.78
2 hr.	9.58
3 hr.	8.37
1 day	4.61
2 days	3.48
4 days	1.69

It has been shown⁸ that treatment of wool with nitrous acid under controlled conditions destroys the free amino groups of wool, the reaction being typical of a primary amine—



Such a reaction, therefore, converts the free amino groups to free hydroxyl groups. Whilst this reaction is not as specific as the reaction with 1-fluoro-2,4-dinitrobenzene, nevertheless the treated wool can be expected to contain more free hydroxyl groups than virgin wool. If sulphation of free hydroxyl groups of serine is occurring, it is to be expected that the newly-formed hydroxyl groups will also react, although the extent will depend on the equilibrium of the reaction between the specific groupings and sulphuric acid.

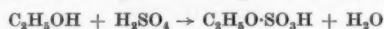
It is seen from Tables I and III that the immediate uptake of sulphate is higher in the case of deaminated wool (13.3% after treatment for 10 min.) than with virgin wool (10.65% under the same conditions).

TABLE III
Sulphate Content of Deaminated Wool

Time of Acid Treatment	SO ₄ (%)
10 min.	13.30
1 hr.	12.50
2 hr.	12.90
3 hr.	13.20
1 day	10.40
2 days	8.57
4 days	4.17
7 days	4.05

From these observations it is obvious that the major preliminary action of sulphuric acid on virgin wool is with the free hydroxyl groups and that the free amino groups play little or no part.

Tables I–III show that continued treatment of any of the three wool samples causes a steady fall in the hydrolysable sulphate content of the undissolved residue. The initial rapid reaction is typical of the reaction of an aliphatic alcoholic group with sulphuric acid to give the sulphate ester, e.g.—

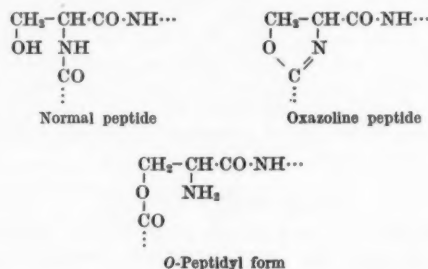


The slow decrease in sulphate content with increased time of treatment is an indication that a secondary, slow reaction takes place at the hydroxyl sites.

Lustig and Kondritzer¹ have previously shown that red hair treated with concentrated sulphuric acid has a reduced serine and threonine content, so it would appear that this secondary reaction could be a selective breakdown of the wool causing a preferential loss of serine and threonine.

It is seen from Table I that, whilst some preferential loss of serine and threonine does occur, the rate of loss is by no means as rapid as would be expected from the fall in sulphate content. Thus after two days the sulphate content falls by 57.7%, whereas the serine and threonine contents fall by 27.4% and 27.2% respectively.

D. F. Elliott¹⁰ showed that, with silk, a reversible shift of the peptide link of serine occurs with the formation of an *O*-peptidyl ester on treatment with concentrated sulphuric acid. It was suggested that the mechanism for this rearrangement was as follows—

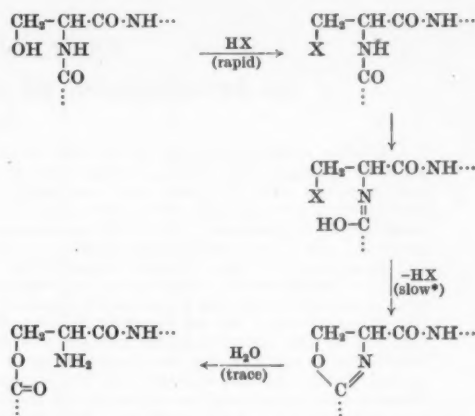


Recently Hille¹¹ has shown that this rearrangement occurs on carbonising wool, the amount of rearrangement being increased by storage under humid conditions¹². However, the amount of conversion is small and, as the overall effect is a slight increase in the number of free amino groups, it cannot explain the resistance of badly carbonised wool to acid dyes.

Unfortunately, as conditions of treatment are different, the amounts of serine amino groups exposed by the rearrangement cannot be correlated with changes in sulphate content observed in the present work.

Roxburgh and Swan¹³ have shown that the rearrangement can occur in wool treated with dry hydrogen chloride gas. It is reasonable to assume that a similar rearrangement is occurring under the present conditions and causing the fall in sulphate content.

It is of interest to note that the reagents used to cause rearrangement (dry hydrogen chloride, concentrated sulphuric acid, and phosphoric acid¹⁴), could all react readily under these conditions with hydroxyl groups to form inorganic esters. It therefore seems possible that the correct mechanism is as follows—



* Alkylation of enolic group with alkyl halide, sulphate, or phosphate.

The authors are indebted to the Wool Textile Research Council for permission to publish this work, and for a grant to two of us (M.E.P.H. and D.H.R.).

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EXTERNAL ADDRESS

An Investigation of the Carbonising of Wool*

H. ZAHN

Wool of crossbred quality, in the form of cloth, was carbonised with sulphuric acid (5% by weight). Part of the baked cloth was rinsed with water at the mill, part was stored in the laboratory in a desiccator over silica gel, and a third part was stored for up to 29 weeks in the conditioning room at 65% R.H. After storage for five weeks and seven weeks respectively, part of the dry and part of the humidified cloth was neutralised. Subsequently the wool was examined for modification by the following methods—alkali solubility, pH of aqueous extract, pyridine extraction, total sulphate, Van Slyke amino nitrogen, and end-group analysis using 1-fluoro-2,4-dinitrobenzene.

The findings led to the following conclusions—(1) The alkali solubility of carbonised wool, if tested soon after preparation and corrected for the sulphuric acid content, is not increased. (2) When wool which has been carbonised but not neutralised is stored under humid conditions a progressive increase in alkali solubility is observed. During dry storage the alkali solubility does not change significantly. (3) Carbonised wool contains about double the number of serine and threonine amino end-groups, whereas the other end-groups of wool are not affected. (4) Dry storage leads to further increase in the number of serine and threonine end-groups and has some effect on the glycine and valine end-groups. (5) Humid storage results in a much faster increase in end-groups. (6) Neutralised wool contains fewer serine and threonine end-groups, whereas the end-groups of the other amino acids remain unchanged or increase slightly. The results are best explained by assuming a partly reversible *N-O*-peptidyl shift on the serine and threonine amino residues during carbonising and neutralisation. Storage of carbonised wool under humid conditions induces irreversible hydrolysis of peptide links involving aspartic and glutamic acids, glycine, alanine, and valine. The practical implications are discussed.

Introduction

"It has been calculated [by W. G. Crewther¹] that carbonising of raw wool can cause a loss of about 10%, in addition to any further loss in processing that may result from the weakening of fibres. The need for research on this process is thus obvious and the number of papers presented, at the first International Wool Textile Research Conference and elsewhere, shows the interest that is being taken"—R. M. Burnett in *Review of Textile Progress*, 9, 379 (1957).

A summary of some recent papers on carbonising has been given elsewhere². The purpose of this paper is to study some questions which have not yet been settled unambiguously—

(1) Does the carbonising of wool increase the alkali solubility? Is the claim of Crewther and Pressley³ correct, viz. that the alkali solubility of carbonised wool, if measured soon after preparation, is not increased?

(2) How long can carbonised wool be stored without its chemical properties being affected?

(3) What influence has humidity on chemical changes taking place in carbonised wool during storage?

(4) What is the chemical mechanism of the reaction of sulphuric acid with serine and threonine peptide bonds?

With the foregoing questions in mind, the present investigations were designed to include a commercial carbonising treatment, as well as a more detailed chemical examination of carbonised samples stored in the laboratory under different conditions.

Experimental

SELECTION AND PREPARATION OF WOOL

A crossbred cloth was obtained from the Tuchfabrik Königsberger, Aachen, with the following construction—

Metric yarn number	Warp 45/2 Weft 44/2
Set	Warp 26–27 ends/cm. Weft 29–30 ends/cm.
Weight of cloth	About 300 g./sq. metre

The cloth was scoured with a solution of Levapon TM (FBy) at 35°C. for 30 min. and then rinsed with cold water.

CONDITIONS OF TREATMENT IN THE MILL

The scoured cloth was carbonised in the dyeing and finishing plant of P. Rouette & Söhne in Aachen on 21st October 1958, using 5% (wt./wt.) sulphuric acid. The temperature during predrying was 63–88°C., and the baking temperature 111–113°C. The soaked cloth passed through the machine in 18 min. The baked cloth was then divided into two parts. One part was immediately placed in a desiccator containing "Blaugel" (silica gel, with cobalt salts as humidity indicator). The other part was rinsed in the plant with water for 20 min. and subsequently treated in a bath containing 1 kg. sodium acetate in 300 litres of water.

STORAGE IN THE LABORATORY

The baked material placed in the desiccator immediately after carbonising was again divided into two parts. One was left in the desiccator, and the other was opened out and hung in a conditioning room maintained at 65% R.H. and 21°C. At intervals of days, weeks, and months samples were taken for analysis. The last samples covered by these investigations had been stored for 7 months.

NEUTRALISATION AFTER STORAGE FOR 5 AND 7 WEEKS

Part of the cloth stored in the desiccator and part of that stored in the conditioning room were rinsed and neutralised in three consecutive baths—

* Paper presented at the I.F.A.T.C.C. Congress held at Church House, Westminster, 16th–18th September 1959.

- Running water for 3 hr.
- 0.2% Sodium carbonate solution at a liquor ratio of 50:1; five dips of 10 min. each
- Running water for 2 hr.

ANALYTICAL METHODS

Alkali Solubility

The procedure of Harris and Smith⁴ and Lees and Elsworth⁵ was applied to duplicate 500-mg. samples (dried at 105°C. for 2 hr.) which had been dissected and cut into 1-cm. lengths of yarn. All results were corrected for sulphuric acid content, estimated by the pyridine method.

pH of Aqueous Extract

The I.W.T.O. method⁶ was employed.

Acid Content

The sulphuric acid content of the wool was determined by the pyridine method of Barritt⁷.

*Total Sulphate Content*²

Samples (each 2 g.) of dried wool were hydrolysed with 20 ml. of 6 N. hydrochloric acid in a sealed glass tube at 105°C. for 24 hr. The sulphate in the hydrolysate was estimated after precipitation with 5% (wt./vol.) barium chloride.

Van Slyke Amino Nitrogen Content

Samples (each 50–60 mg.) of dried wool were treated with sodium nitrite and acetic acid in the apparatus for continuous evolution of nitrogen described by Kainz⁸, the nitrogen evolved being plotted against time of reaction. The treatment was continued for up to 340 min. By graphic extrapolation the amino nitrogen content of the wool samples at zero time was obtained.

*Amino End-Group Determination with 1-Fluoro-2,4-dinitrobenzene*⁹

The procedure described by Steuerle and Hille¹⁰ was used. These authors have found 6,6-nylon powder to be a very suitable adsorbent for a complete separation of dinitrophenylated (DNP) amino acids by column chromatography in one run, using phosphate buffer of pH 6.8 as eluent at 60°C. during the chromatography. They also succeeded in completely separating the seven DNP amino acids isolated from DNP wool, as is seen in Fig. 1, which shows the chromatogram of the ether-soluble DNP amino acids of wool.

Samples (each 1 g.) of carbonised or neutralised wool were dinitrophenylated at a pH of 5.5–5.8. (This pH differs from that normally used, the lower pH being necessary in order to retain some of the *O*-peptidyls, which are converted to normal *N*-peptidyls at higher pH values¹¹.) A full account of the end-group estimation of carbonised wool samples has been given by Hille¹².

Results

CARBONISING AND RINSING IN THE PLANT

The results of chemical tests on the cloth carbonised and rinsed in the dyeing and finishing plant are given in Tables I and II and Fig. 2. The carbonised sample contains 7% sulphuric acid or

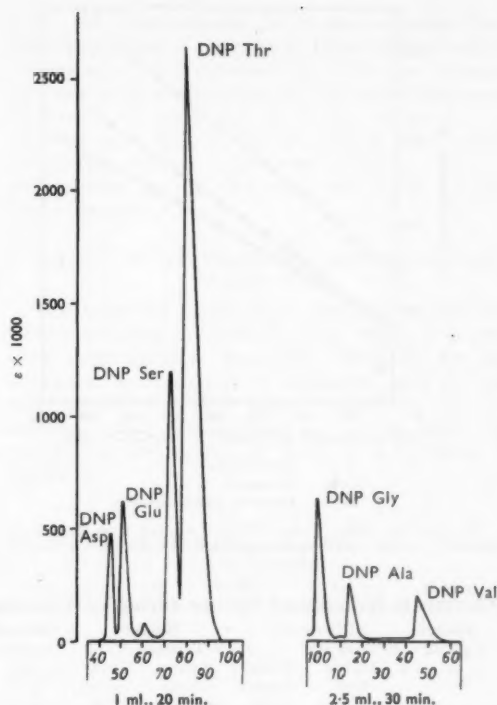


FIG. 1—Separation of Seven Ether-soluble DNP Amino Acids, isolated from 0.5 g. DNP wool

1.54 m-equiv./g. Autotitration up to pH 5 gave a consumption of 1.57 ml. of 0.1 N. caustic soda.

On comparing the results it is evident that rinsing with water and then treating with sodium acetate is not very effective as a method of neutralising the wool, for the rinsed cloth still contains 1% titratable sulphuric acid.

TABLE I
Piece Carbonising

	Scoured	Baked	Rinsed (Na acetate)
pH	7.6	2.0	3.8
H ₂ SO ₄ , % ...	—	7.0	1.0
Total sulphate, % ...	0.78	7.6	1.6
Alkali solubility (corr.), % ...	12.7	12.8	13.8
Van Slyke N, % ...	0.16	0.30	0.18

The alkali solubility of the baked cloth sample after correction for 7% sulphuric acid is the same as that of the scoured cloth before carbonising. This finding strongly supports the statement by Crewther and Pressley³ that the alkali solubility of carbonised wool, if tested soon after preparation, is not increased.

As is seen from Table I and Fig. 2, the Van Slyke nitrogen content of the baked sample is nearly double that of the untreated sample, whereas the rinsed and partially neutralised cloth sample gives much less Van Slyke nitrogen.

The results of the end-group analysis using 1-fluoro-2,4-dinitrobenzene on the same samples are given in Table II.

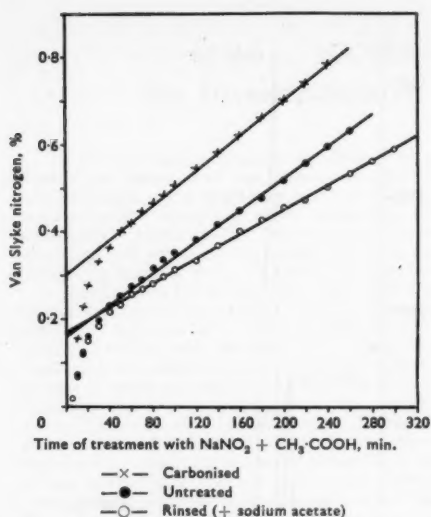


FIG. 2—Van Slyke Amino Nitrogen evolved from Untreated, Carbonised, and Rinsed Cloth

TABLE II
Changes in N-Terminal Groups during Carbonising

Amino Acid	Untreated		Baked		Rinsed μmoles per g. of wool
	N-Terminal	% of	N-Terminal	% of	
	Amino	Total	Amino	Total	
	Acid	Amino	Acid	Amino	
	μmoles/g. of wool	Acid which is	μmoles/g. of wool	Acid which is	
		N-Terminal		N-Terminal	
Aspartic acid	0.20	0.039	0.23	0.045	0.25
Glutamic acid	0.26	0.025	0.25	0.024	0.34
Serine	2.34	0.27	6.68	0.77	5.80
Threonine	4.69	0.84	6.51	1.16	5.81
Glycine	1.48	0.19	1.11	0.14	1.76
Alanine	0.52	0.12	0.51	0.12	0.56
Valine	0.48	0.11	0.53	0.12	0.53
Total	9.97		15.82		15.05

It is seen from Table II that, during carbonising, many new end-groups are formed consisting of serine and threonine only. However, only very few new end-groups consisting of aspartic acid and valine can be found.

The rate of increase in serine end-groups during carbonising is 50 times that of valine end-groups. The increase in threonine end-groups is 32 times as fast as that of valine end-groups. The total increase in end-groups is found to be about 6 micromoles per gram of wool.

Rinsing has the opposite effect on serine and threonine end-groups, which are diminished, compared with all the others, which remain constant or increase slightly.

DRY AND HUMID STORAGE IN LABORATORY

The results of the investigation of the effects of dry and humid storage of unneutralised carbonised cloth samples are illustrated in Fig. 3 and 4.

Fig. 3 shows that storing carbonised wool under dry conditions (in the desiccator) does not affect the alkali solubility very much, whereas storing it in the conditioning room results in a progressive increase in alkali solubility.

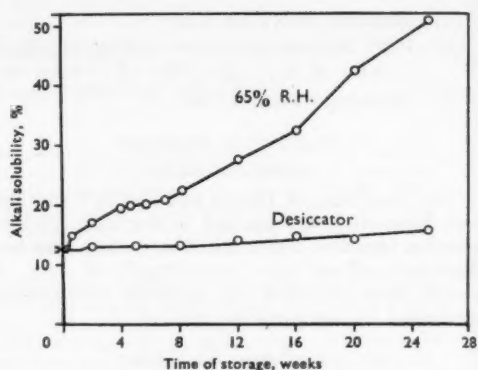


FIG. 3—Alkali Solubility of Carbonised Cloth Stored Dry and Humid

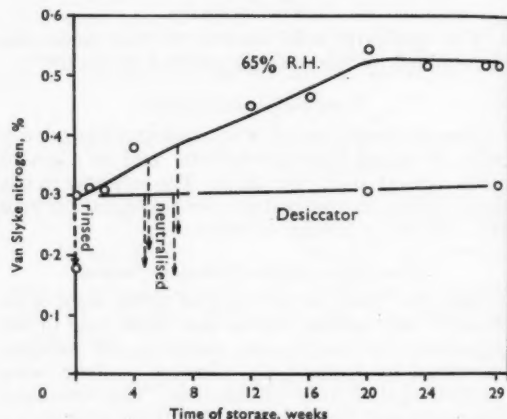


FIG. 4—Van Slyke Primary Amino Nitrogen evolved from Carbonised Cloth stored Dry and Humid. The dotted vertical lines show the changes caused by neutralisation after 5 and 7 weeks' storage

Fig. 4 shows a similar difference between the effects of dry and humid storage. The Van Slyke nitrogen content of wool stored dry is only slightly increased, even after 29 weeks, whereas humidity causes increased values after only two weeks. At the end of the period covered by testing, an increase of 0.2% in the amino nitrogen content of the humidified specimen is observed, equivalent to an increase of 140 micromoles of amino groups per gram of wool. Since 1 g. wool contains about 8,000 micromoles of amino-acid residues, this means that 1 in every 55 amino-acid residues has a free amino group, and the average equivalent weight of carbonised wool after 29 weeks of humid storage is only $55 \times 110 = 6,050$.

The results plotted in Fig. 4 indicate that storing acidic wool at 65% R.H. results in a progressive splitting of peptide bonds, which explains the increased alkali solubilities. From this it is clear that storage of carbonised wool, if necessary, should be done under dry conditions. Increased alkali solubilities or Van Slyke nitrogen figures encountered in practice can be explained by too long storage of carbonised wool under humid conditions.

The results of end-group estimations by the Steuerle and Hille¹⁰ procedure using 1-fluoro-2,4-dinitrobenzene for samples of cloth which have

been stored for 7 weeks are given in Table III. They show that dry storage produces about 3 micromoles of new amino groups per gram, whereas humid storage more than doubles the proportion of amino end-groups present in baked wool.

TABLE III
N-Terminal Group Contents
(μ moles per g. wool)

Amino Acid	Baked	Stored for 7 weeks	
		Desiccator	65% R.H.
Aspartic acid	0.23	0.31	0.69
Glutamic acid	0.25	0.35	0.62
Serine	6.68	8.24	17.01
Threonine	6.51	7.32	12.17
Glycine	1.11	1.58	3.07
Alanine	0.51	0.55	0.91
Valine	0.53	0.63	0.75
Total	15.82	18.98	35.22

It is of interest to relate the absolute figures found to the total amount of each amino acid combined in one gram of wool, and the results of such calculations are given in Table IV.

Again it is seen that, during storage, the serine and threonine peptide links are attacked much faster than the other peptide links, but the rate is no longer 50:1 (see Table II) but only 3:1 compared with the second fastest splitting bond, glycine. During storage, therefore, the reaction of the serine and threonine is not as specific as during carbonising alone. For this reason it is concluded that, besides the specific changes taking place in the serine and threonine peptide bonds, some normal hydrolysis of other peptide bonds must occur. Nevertheless, it is of interest that no new ether-soluble amino end-groups have been observed other than those occurring in untreated wool. This may mean that these amino acids are much more sensitive than the others, so that they form end-groups as a result of some preliminary attack, and are not true peptide-chain end-groups.

It is not possible to compare the results of the detailed amino end-group analysis using 1-fluoro-2,4-dinitrobenzene with those obtained by the Van Slyke method, because the two methods operate at different pH values, and with the latter method amino groups of diaminocarboxylic acids, e.g. lysine, are involved. After seven weeks' storage the Van Slyke method gave an increase in amino nitrogen of about 0.07%, or about 45 micromoles per gram of wool, whereas Sanger's reagent gave an increase of only 20 micromoles. Unfortunately,

only the ether-soluble DNP amino acids have been estimated. Changes in ether-insoluble DNP amino acids may decrease the difference between the two methods by about 25 micromoles per gram of wool. It must also be borne in mind that Steuerle and Hille¹⁰ did not correct their values for losses during hydrolysis. Finally, dinitrophenylation at pH 5.5 will not block all free amino groups.

EFFECT OF NEUTRALISING CARBONISED AND STORED WOOL

The result of neutralising cloth stored for five weeks is shown in Table V, from which it is seen that neutralisation was fully effective, for the sulphuric acid content is negligible, and the pH near neutrality. The alkali solubilities did not increase after neutralisation, as is seen by comparing the figures of Table V with those of Table II.

TABLE V
Neutralisation of Carbonised Wool after Storage for 5 weeks

Storage	pH	H ₂ SO ₄ (%)	Alkali Solubility (%)	Van Slyke Amino N (%)
Dry	7.6	0.1	15.3	0.18
Humid	7.5	0.1	21.9	0.21

The Van Slyke amino nitrogen decreases considerably after neutralisation, especially after dry storage (see Fig. 4).

In order to investigate in detail the origin of this decrease in amino group content of neutralised wool, end-group analyses were made of neutralised wool samples stored for seven weeks (see Table VI).

TABLE VI
Effect of Neutralisation on the N-Terminal Groups of Carbonised Wool stored for 7 weeks
(μ moles per g. wool)

Amino Acid	Desiccator Sample	Conditioned Samples		
	Before	After Neutralisation	Before	After Neutralisation
Aspartic acid	0.31	0.36	0.69	0.51
Glutamic acid	0.35	0.44	0.62	0.61
Serine	8.24	4.38	17.01	9.04
Threonine	7.32	5.85	12.17	6.99
Glycine	1.58	1.94	3.07	3.06
Alanine	0.55	0.64	0.91	0.93
Valine	0.63	0.68	0.75	0.80
Total	18.98	14.29	35.22	21.94

TABLE IV
Change in N-Terminal Groups in Carbonised Cloth during Storage
(% of total amino acid which is N-terminal)

Amino Acid	Baked	Stored Dry			Stored Humid		
		Absolute Value	Actual	Relative*	Absolute Value	Actual	Relative*
Aspartic acid	0.045	0.061	0.016	1.6	0.135	0.090	3
Glutamic acid	0.024	0.034	0.010	1	0.060	0.036	1
Serine	0.77	0.95	0.18	18	1.96	1.19	33
Threonine	1.16	1.30	0.14	14	2.17	1.01	28
Glycine	0.14	0.20	0.06	6	0.39	0.25	7
Alanine	0.12	0.13	0.01	1	0.22	0.10	3
Valine	0.12	0.15	0.03	3	0.17	0.05	1.5

* Relative to glutamic acid = 1

It is seen that the amino end-group content of all amino acids other than serine and threonine either remains constant or increases as a result of neutralisation. Only the amino end-groups of serine and threonine decrease considerably. This difference is illustrated diagrammatically in Fig. 5, where for clarity only changes in *N*-terminal serine and glutamic acid are shown.

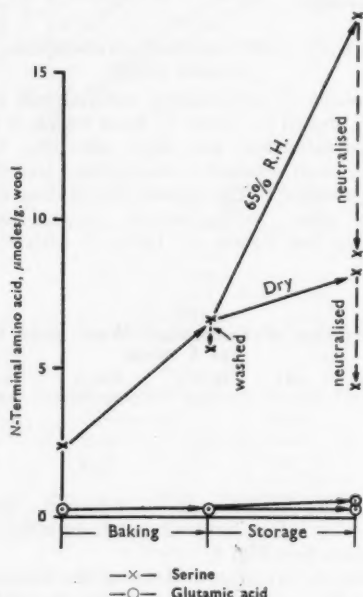


FIG. 5.—Changes in Amino End-group Contents for Serine and Glutamic Acid after Baking, Storing, and Neutralising

The Sanger method confirms the result of the Van Slyke analysis: neutralising carbonised wool decreases the number of amino groups. The aggregate of *N*-terminal amino groups in the untreated cloth has been found to be about 10 micromoles per gram, rising to 16 after carbonisation, then to 19 after dry storage for seven weeks, and decreasing to 15 micromoles per gram after neutralisation.

On comparing the behaviour of dry and humidified wool when neutralised, it is seen that wool stored under humid conditions does not reach the same low figures as wool stored under dry conditions, viz. 9.04 against 4.38 micromoles serine per gram of wool. The power of recovery must therefore have been impaired.

Discussion

The results described above, as well as some other results¹³ omitted here for the sake of clarity, enable definite answers to be given to the questions posed at the beginning of this paper—

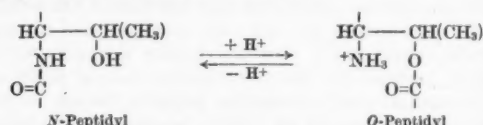
(1) The carbonisation of wool does not immediately increase its alkali solubility significantly, as is shown if the latter is determined soon after baking. The claim of Crewther and Pressley³ is confirmed.

(2) Carbonised wool can be stored for many weeks without its chemical properties, e.g. alkali solubility and amino nitrogen content, being

affected, provided that moisture is completely excluded. Under normal humidity conditions it cannot be stored for longer than two days.

(3) Storage of carbonised wool at room temperature with free access of moisture results in a progressive increase in alkali solubility starting after 4 days, as well as a steady increase in amino end-groups. The power of recovery, as far as a decrease in serine and threonine amino end-groups after neutralisation is concerned, is impaired when carbonised wool is stored under humid conditions.

(4) The chemistry of the changes undergone by the serine and threonine peptide groups, viz. a specific fission during carbonising and storage under acidic conditions, and a specific decrease in free amino groups after neutralisation, can best be explained by an *N*-*O*-peptidyl shift. Interest in this early-investigated reaction of protein chemistry¹⁴ has in recent years been revived by the work of Desnuelle and Casal¹⁵, Desnuelle and Bonjour¹⁶, Elliott¹¹, Chibnall and Rees¹⁷, and Edman and Josefsson¹⁸. The last-mentioned authors adduced evidence for a reversible *N*-*O*-peptidyl shift occurring in lysozyme and ribonuclease during inactivation in formic acid, and reactivation during neutralisation. The *N*-*O*-peptidyl shift is formulated as—



In fact, it was Edman and Josefsson's work that induced our own study of wool carbonisation¹³, for we wished to know whether or not a reversible *N*-*O*-peptidyl shift occurs under the conditions of commercial carbonising and neutralisation. This, in fact, has been proved. On the other hand, it must not be overlooked that only a very small proportion of the serine and threonine peptide links are involved. Carbonising increases the number of free serine amino groups from 0.27 to 0.77%, expressed as a percentage of the total serine content, and for free threonine from 0.84 to 1.16%. As far as reversibility is concerned, this property is not very clearly distinguishable with wool. From Fig. 5 it is seen that the original values for serine and threonine amino end-groups are not attained, and reversibility is not greater than 60%.

Our hypothesis of an *N*-*O*-peptidyl shift occurring under commercial carbonising conditions has been confirmed by Roxburgh and Swan¹⁹. Their work on the *N*-*O*-peptidyl shift in proteins and the implications of this reaction for the carbonising process has indicated the occurrence of a substantial extent of migration in serine residues in wool heated at 105°C. in dry hydrogen chloride. In the conditions of laboratory carbonising experiments there is evidence that sulphuric acid causes similar reaction to a more limited extent (not greater than 10%). Their analytical methods were (a) colorimetric ninhydrin determination of free amino groups in proteins and (b) chromatographic determination of amino acids (serine and

threonine) after blocking the NH_3^+ groups exposed by anhydrous acid treatment. Acyl migration is suggested as the cause of such exposure, since on subsequent neutralisation to pH 7 or (especially) 8 the increase in amino groups and decrease in serine and threonine is markedly reduced.

The hypothesis of *N-O*-peptidyl shift explains some of the mill experience and the results of the intensive research on carbonising which is proceeding in various institutes—

(a) Preheating before baking results in low alkali solubility, because in the absence of moisture no irreversible hydrolysis occurs. The sulphuric acid causes only a peptidyl shift, which can be reversed, when neutralisation follows soon after baking.

(b) Storing carbonised wool under humid conditions increases the alkali solubility and causes damage in the wool, because in the presence of moisture the *O*-peptidyl or ester forms of the peptides in wool are hydrolysed by the acid present. This hydrolysis reduces the number of *O*-peptidyl groups which can be converted to the normal peptide form.

(c) Carbonised and carefully neutralised wool must be handled with care during further processing (bleaching, dyeing, etc.), because even under the most favourable conditions there are always a number of permanently broken peptide bonds in carbonised and neutralised wool. The sulphuric acid combined in the wool protein is not split off during neutralisation, but only after complete hydrolysis. Carbonised wool is therefore more reactive than untreated wool.

SOME PRACTICAL IMPLICATIONS

The Sanger technique of amino end-group determination, even in the modified and elegant procedure of Steuerle and Hille¹⁰, will remain a method for research institutes only for a long time to come.

The Van Slyke method of amino nitrogen estimations, owing to its simplicity, has been proved a valuable tool in checking the effectiveness of neutralisation, and the changes taking place in acidic wool during humid storage.

The well known method of alkali solubility measurement is very useful for testing carbonised wool. If a commercial sample of carbonised wool gives high alkali solubility figures, e.g. $> 20 \pm 2\%$, there are various possible explanations—

(a) The original wool has had a high alkali solubility before carbonisation and neutralisation (noils, skirtings, crutchings, chemically pretreated wool).

(b) Predrying before baking has not been effective³.

(c) The carbonised wool has not been rinsed and neutralised at once, but stored under humid conditions for more than 2–4 days.

(d) The carbonised wool has undergone an additional treatment, e.g. bleaching. It is well known that bleaching and other oxidising treatments increase the alkali solubility considerably.

It is unfair to blame the carbonising plant for an increased alkali solubility if one insists on wool wastes with high burr contents being carbonised very heavily and also bleached.

Normally the commercial carbonising plants seem to handle their material quite well, because tests on 18 typical loose wool samples from the wool trade gave reasonably low alkali solubility figures²⁰. Only one sample exceeded 30%, and this consisted of carbonised and bleached crutchings.

* * *

The author thanks Dr. E. Hille for putting at his disposal his results of amino end-group estimations, as well as his Baden-Baden lecture. Further, he gratefully acknowledges the assistance of Fräulein Gesine Töpert, Fräulein Marly Hirtz, and Frau Helga Schüssler in carrying out the chemical tests. Thanks are due to the International Wool Secretariat and the West German Bundeswirtschaftsministerium for research grants. The firm of Rouette & Söhne at Aachen made available the carbonising equipment.

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(MS. received 2nd June 1959)

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CORRESPONDENCE

The Publications Committee does not hold itself responsible for opinions expressed by correspondents

Assessment of Light Fastness Exposures

A statistical investigation into the assessment of light exposures¹ showed that the standard deviation among experienced assessors varies from 0.22 to 0.72, the highest values (indicating the least degree of agreement) occurring with specimens which fade off-tone. The exposures for this investigation were obtained by Method 2 of the Standard Method, *B.S. 1006:1955*, in which the progressive covering is governed mainly by the amount of fading on the *standards*: this method is the one most widely used, as it enables one set of standards to be used for a large number of specimens of unknown and variable light fastness.

It was considered possible that had Method 1 been used, in which the covering is governed by the amount of fading on the *specimen*, better agreement might have been obtained, so to test this possibility the two fabrics which gave rise to the greatest amount of disagreement were re-exposed by Method 1 and these exposures assessed by 30 of the experienced assessors who had taken part in the earlier investigation. The results obtained by elementary statistical analysis are as follows—

Specimen	Mean Light Fastness		Standard Deviation	
	Method 1	Method 2	Method 1	Method 2
2	2.1	2.0	0.4	0.7
7	4.8	4.4	0.2	0.5

These figures clearly indicate a much greater degree of agreement and show the wisdom of the Light Fastness Subcommittee in stating that "Method 1 is the ideal method and shall be used in cases of dispute".

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27th January 1960

¹ McLaren, K., *J.S.D.C.*, **75**, 597 (1959).

Indiscriminate Use of Fluorescent Brightening Agents

I read with interest the recent letters on fluorescent brightening agents by Ward and Blackburn¹ and by Kornreich².

There is no doubt that fluorescent brightening agents are being applied indiscriminately today in an attempt to obtain "whiter than white". Only in organisations having their own laboratories is it possible to be fully aware of their presence. One finds them on nylon, wool, cotton, and rayon. I have even detected them on fabrics intended for drapings. Since the majority of these products have only moderate light fastness, many whites begin to change to drab tones fairly soon after exposure to daylight. A survey recently made in one store showed that, of seven different-quality, white spun-rayon cloths on sale, all contained this optical finish. Fading tests (*B.S. 1006:1955*) carried out on these cloths showed that six had light fastness gradings of 4.

Similarly, there is scarcely a washing powder on the market which does not contain a fluorescent brightening agent. For washing whites this may be a good thing, but not for coloured goods, if it is desired to retain the original shade of the article. No doubt there is a good reason for using this type of product, but more discrimination is needed in its application.

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12th February 1960

¹ Ward, J. S., and Blackburn, D., *J.S.D.C.*, **75**, 493 (Oct. 1959).

² Kornreich, E., *ibid.*, **76**, 37 (Jan. 1960).

Colour Index**Additions, Amendments, and Corrections**

Resulting from conversations held by Messrs. W. D. Appel and G. Paine as delegates of the A.A.T.C.C. with the Society's Finance and General Purposes Committee and *Colour Index* Editorial Board, the quarterly issue in the *Journal* and the *American Dyestuff Reporter* of lists of Additions and Amendments has ceased. Instead these lists are being issued quarterly only to those subscribing for them. The subscription is £2 per annum and further details regarding it may be obtained from

the offices of the Society or of the Association. In accordance with the undertaking given in Vol. 1 of the *Colour Index* 2nd Ed. corrections to existing entries continue to be published in the *Journal* and in the *American Dyestuff Reporter* and such corrections also form part of the lists of Additions and Amendments issued to subscribers. The first list of corrections appeared on p. 40 of the January 1960 issue of the *Journal* and the second list appears on p. 236-7 of the present issue.

Notes

Historical Records Committee

Mr. W. S. Stansfield's Gift of his Notebooks for 1901-9

Mr. W. S. Stansfield has presented two note books to the Historical Records Committee. They were compiled by him in the years 1901-1909 whilst he worked in Bowling Dyeworks—Ripleys, Bradford. The books give a wide variety of data on recipes, methods, processes, costs, and prices. They are valuable to the dyeing historian and of great interest to any piece dyer.

The first book (1901-1903) deals mainly with silk fabrics. The caustic degumming of Gloria (silk warp, wool weft) as done in "K" Department is described thus: "(1) crab light, (2) steam, (3) dry and gas, (4) scour at width and dry, (5) wet out and gum extract, viz. immerse for 7 min. in NaOH at 44°Tw., temperature not higher than 45°F., neutralise at once with H₂SO₄—soap, scour, dry, stove and dry". There are grey and finished patterns of the Gloria fabric thus scoured. The grey is rough, dirty, and shaggy, the other is smart, clean, and flat with the silk white, and the wool weft strong. A lilac pattern in the same quality was dyed with Acid Violet 3BN in an acid bath and has a most attractive sheen and crisp warm silk handle.

There is another process for black on Glorias without degumming. The instructions are a model for any apprentice, because they are brief yet indicate the danger spots, e.g. "(1) Crab (not more than 2 pieces on a roll) without top weight or tension, roll out as easy as possible and pull out in width . . . (2) Steam 15 min., steaming can must have a covering of canvas 1" thick—stand on can until cold . . . Bag, dye with Gloria Black". The large finished pattern shows a good black, clean flat finish, full handle. There is no trace of moiré or excessive shine, because these faults were prevented by the precautions described. The dangers of shininess and water marking have still to be guarded against today, with blacks and dark dyeings on man-made fibre fabrics—and the young dyer/finisher of such might well take as an exemplar this thoroughbred Gloria of 1901.

There are several descriptions of continental dyeing processes ascribed to W. Korten of Como, Italy. The most interesting of these describes a method of cross dyeing silk piece goods. The yarn for the weft is tin loaded, mordanted with tannic acid-tartar emetic. The warp yarn is in gum. The fabric woven from these yarns is boiled-off in the usual way, bagged, dyed in beck, one bath, strongly acidified acetic acid. Basic colours dye the mordanted weft and reserve the pure silk warp which is dyed in same bath with acid or direct dyes reserving the mordanted weft.

The patterns of cross-dyed satin brocade are in lovely classic colours very similar to the Celanese and viscose jacquards dyed by me when an apprentice at Stockbridge, Keighley, in 1924. A typical example is cerise/gold. In the 1901 recipe it is dyed with Auramine O and Acid Magenta in one bath. The Celanese and viscose

of 1924 was dyed with Azo Yellow and Pink BK (Chlorazol). Mr. Stansfield's dyed patterns remind us that the classic styles and colours always stay; they are continually reproduced in new fibres and new dyes.

The second book 1906-1909 is more mature. There are fewer mounted patterns, and more minute detail of processes. Parchmentising (Oct. 1908) is a good example of the book's merits. "This process is applicable to unions (cotton and wool) and all cotton goods. It swells and softens the cotton without shrinkage, increases affinity for direct dyes, making it possible to dye unions in one bath in shades and qualities hitherto unaccomplished." There is a careful drawing of the machine used, with legend examples, e.g. "ebonite nip rollers with simple levers; wood cistern, lead lined, with lead refrigeration pipes; the speed is 30 yards per minute, from entry to delivery takes 3½ minutes; the cost of machine, without refrigerator, is £600."

Crêpon mercerising is fully detailed "crêpons for mercerising consist of a mohair or worsted warp for the face, backed with a cotton warp and cotton weft; the cotton weft acting as a binder for the face warp." It is described as a Thornton, Hannam & Marshall process and could be used again today from this clear description.

The famous Cravenette and the Ripley proofing methods are described. They were difficult to apply to cream wools, e.g. Imperials, Coverts "owing to dirt and proofing stains". A simpler proofing was used for these fabrics—"after stoving and drying give 6 ends at a pad through acetate of alumina 2°Tw., and dry without rinsing. This proof is not near so good as either Cravenette or Ripley proof, but when one considers how seldom a cream coat will be taken out whilst raining, the proof fulfils all requirements". This is a far cry from modern rainwear or outerwear requirements! Yet it was the best that could be done then; just as the best disperse blues were spoilt by a whiff of burnt gas fumes until a few short years ago.

The recipes for blacks and navys on union serge show use of standing baths, 25% of dye being saved by this method of vessel dyeing. There was risk of crimping in rope dyeing; good results were obtained by jigger dyeing, but with risk of bronzing "removed by boiling-water wash".

A dodge of those days is described in the dyeing of commercial Indigo as practised by Wilfred Ward of Elland on worsted coatings and woollens. The method "(1) chrome, (2) bottom with Gallocyanine and Alizarine Red, (3) top in Meister's hyposulphite vat. By this method a good nitric spot is given with little Indigo."

There are several pages of costs and price lists, e.g. "pressing prices paid by Grandages, April 1909—linings and Italians twice pressed—up to 46 yards 6½d. per piece, up to 46/50 yards 8½d. per piece, up to 56/60 yards 9d. per piece." The price

for dyeing and finishing Lustre Brills 33/36" was 6/0d. per piece of 40/45 yards in 1904. Schreiner finish on aniline black was 1½d. per yard extra on 8/4 cotton Italians. There are "monthly summary of wages cost" for the various departments at Ripleys. And a breakdown of dyehouse accounts shows 5% for D. & K. and 29% for profits!

Summer School 1960

The Society's Summer School for 1960 is to be held in Manchester, at the College of Science and Technology. The theme is rather different from that of recent Schools in that it is not specially devised with the requirements of the Associateship examination in mind, since these are now being more generally catered for in regular classes at a number of centres. Because of its great importance and the fact that organised information is not widely available, the subject will be Fastness and Fastness Testing, various aspects of the textile and non-textile applications of which will be discussed. A full programme of lectures, demonstrations, practical work, works visits, and social activities is well on its way to completion and it is hoped to announce details very soon.

Accommodation has already been booked at the new Woolton Hall of Residence of Manchester University.

Registration will be on Saturday, September 10th, and lectures, etc., will extend from September 12th to 16th.

Golden Jubilee of the Textile Institute

This year is the Golden Jubilee of the Textile Institute which was founded in Manchester in 1910. To mark the occasion the President of the Society, Mr. John Boulton, has sent to the President of the Textile Institute, The Rt. Hon. the Earl of Derby, M.C., the following message—

The Society of Dyers and Colourists, its Officers and Council, have noted with pleasure that in 1960 the Textile Institute will reach its 50th birthday. The Society sends its warmest felicitations on this Jubilee. The past fifty years have seen the Institute grow into an organisation which, in the excellence of its publications, its conferences, and its educational activities in the field of textile technology, is wholly admirable.

May the next fifty years be equally inspired and equally fruitful.

With best wishes

JOHN BOULTON

President

Second Quinquennial Wool Textile Research Conference

Fibre Science

Harrogate, 18th-27th May 1960

Full details regarding this international conference, at which over 70 papers presented by research workers from 13 different countries will be discussed, are now available from the General Secretary, The Textile Institute, 10 Blackfriars

Street, Manchester 3. The general theme of the conference will be Fibre Science. The conference will be followed immediately by the Jubilee Conference of the Textile Institute (see below).

R. A. PEEL

Jubilee Conference of the Textile Institute London, 30th May to 3rd June 1960

As part of the celebration of its Golden Jubilee the Textile Institute is holding its Jubilee Conference in London. This Jubilee Conference is intended to provide an opportunity for scientists of outstanding ability to direct attention to the general trends of scientific thought and their application to industry generally. Opportunity will also be given to leading textile scientists to show how these ideas are affecting textile research and development. Particulars regarding this Jubilee Conference are available from the General Secretary, The Textile Institute, 10 Blackfriars Street, Manchester 3.

Silver Jubilee of the Canadian Association of Textile Colourists and Chemists Ontario Section

The C.A.T.C.C. Ontario Section held its Silver Anniversary Annual Banquet on Saturday, 6th February 1960, when the following cable was received—

Congratulations and every good wish for a happy and successful evening in celebration of your Association's 25 years' jubilee. Greetings. John Boulton, President, The Society of Dyers and Colourists, England.

Werner von Bergen, F.S.D.C. awarded the 1960 Harold DeWitt Smith Memorial Medal

The American Society for Testing Materials has chosen Werner von Bergen, a Fellow of the Society, as the 1960 recipient of the Harold DeWitt Smith Memorial Medal. Mr. von Bergen, who received his academic training in Switzerland before he emigrated to the United States, is a well known authority on wool and its processing. He had already received in 1952 the Olney Medal of the A.A.T.C.C. of whose Research Council he has long been an active member.

Eighth London Lecture

The Eighth London Lecture will be delivered by Mr. S. J. R. Leeming (Samuel Courtauld & Co. Ltd., Halstead), on Friday, 21st October 1960, in the Waldorf Hotel, London, his subject being Colour and Design in Dress Fabrics.

International Association for the Protection of Industrial Property

XXIVth Congress, London, 30th May to 4th June 1960

This international association is concerned with patents and trade marks and similar rights (known internationally as rights in "industrial property"). Its twenty-fourth Congress will be held in London from Saturday, 28th May to Saturday, 4th June 1960, under the patronage of H.R.H. The Duke of Edinburgh and the presidency of Sir John Hansbury-Williams, C.V.O. It is expected that over 600 members from 35 countries will attend. An item of particular interest on the agenda is the work to be done in obtaining some harmonisation of international laws and practice for patents, trade marks, and industrial designs.

During the Congress members and their wives will be given an official reception by Her Majesty's Government at Lancaster House. There will also be a gala performance at the Royal Opera House and a banquet at the Royal Courts of Justice, followed by a ball in the Middle and Inner Temple Halls.

Further particulars are obtainable from the Secretary to the Organising Committee, Mr. H. C. Miller, XXIVth Congress A.I.P.P.I., 16 St. Martin's Le Grand, London E.C.1, P.O. Box 218.

Symposium on Physical, Chemical, and Biological Methods in the Study of High Molecular Weight Carbohydrates, Edinburgh 12th-14th July 1960

The above symposium is being sponsored by the Chemical Society. The full programme will be available in April 1960 and copies will be sent to all who apply to the General Secretary, The Chemical Society, Burlington House, London W.1, before 31st March 1960.

Training of the Industrial Physicist

The Education Group and Midland Branch of the Institute of Physics are holding a joint conference on the above subject on Thursday and Friday, 21st-22nd April 1960, in Birmingham. Detailed programmes and registration forms are available from the Secretary, The Institute of Physics, 47 Belgrave Square, London, S.W.1.

Powders in Industry: Properties and Principles of Application

Symposium to be held on 29th-30th September 1960 by the Surface Activity Group of the Society of Chemical Industry

This symposium will be held at the Royal Institution, London. It will be divided into four sections. A—Principles of production, B—Properties of powders, C—Properties of powders utilised in industrial fields, and D—Principles of application and problems for the future. In Section C there are four papers dealing with pigments and one each with textiles and paper.

Registration fee for the symposium is £4 0s 0d. (£2 10s. 0d. for members of the Society of Chemical Industry), this fee includes the cost of preprints.

Further information can be obtained from the Honorary Secretary, Surface Activity Group, Society of Chemical Industry, 14 Belgrave Square, London, S.W.1.

Laboratory and Materials Exhibition London, 20th-23rd June 1960

This exhibition, to be held in the Royal Horticultural Society's New Hall, Westminster, London, S.W.1, will be the first time there has been such a national show devoted solely to laboratory supplies. In addition to the exhibitors' stands a programme of special lectures on various scientific subjects is being arranged. There will also be film shows dealing with aspects of laboratory work and demonstrations of glass-blowing and other laboratory techniques. Further details will be supplied by the Exhibition's Press Officer, Janet Wheaton, 6 Mercier Road, London, S.W.15.

Russian Chemical Journals

The Chemical Society with the assistance of the Department of Scientific and Industrial Research is about to publish cover-to-cover translations of the Russian Journal of Physical Chemistry (*Zhurnal Fizicheskoi Khimii*) and Russian Chemical Reviews (*Uspekhi Khimii*). The first of these will commence with the July 1959 issue and is now available, translation of the other journal will commence with the January 1960 issue which should be available in April 1960. All inquiries should be addressed to the sole distributors: Cleaver-Hume Press Ltd., 31 Wright's Lane, London, W.8.

India adopts the Metric System for Control of Imports and Exports

Commencing in August 1960 India will use the metric system of weights and measures for control of her import and export trade.

Library of the Chemical Society

The above library, which is open to members of our Society (see J.S.D.C., 76 (Jan 1960) 3) will be closed on Whit Monday and Tuesday, 6th and 7th June 1960 and will reopen at 9.30 a.m. on Wednesday, 20th April 1960.

Death of Member

We regret to report the death of Dr. A. R. Macormac of the University of Alabama, who had been a member of the Society for over a quarter of a century.

Meetings of Council and Committees March

Council—2nd
Finance and General Purposes—2nd
Publications—15th
Light Fastness Subcommittee—15th
Disperse Dyes Subcommittee—18th
Diplomas—30th
Disperse Dyes—30th

COLOUR INDEX

Corrections

April 1960

VOLUME 1

Page					
1104	C.I. Acid Red 30	transfer to	Java Light Red BL	Vond	
1117	C.I. Acid Red 57	for read	C.I. Acid Red 37		
1135	C.I. Acid Red 99	transfer	Propolan Red 3GP	ICI	
			Propolan Red 3GX	ICI	
		transfer to	BenzyI Fast Red BG	CAC, Ciba	
	C.I. Acid Red 99	transfer to	C.I. Acid Red 114		
1151	C.I. Acid Red 133	transfer to	Perlan Red RS	Vond	
			C.I. Acid Red 114		
		transfer to	BenzyI Fast Rubine 2B	CAC, Ciba	
			Brilliant Milling Red B	NAC	
			Polar Brilliant Red B	Gy	
			Sulfonine Brilliant Red B, BG	S	
		to	C.I. Acid Red 249 (new entry)		
1163	C.I. Acid Red 167				
	under "The following brands are similar"	transfer to	Perlan Red B	Vond	
1199	C.I. Acid Violet 17	for read	C.I. Acid Red 128		
1301	delete C.I. Acid Blue 164		Hispacid Violet S4BN	RBM	
	transfer dye and all information to		Hispacid Violet X4BF	RBM	
1375	C.I. Acid Black 1	transfer to	C.I. Acid Blue 161		
1437	delete C.I. Mordant Orange 9		Java Blue Black 10BS	Vond	
	transfer dyes and all information to		C.I. Acid Black 41		
1447	delete C.I. Mordant Orange 31		C.I. Mordant Orange 3		
	transfer dye and all information to		C.I. Mordant Orange 37		
1459	delete C.I. Mordant Red 18		C.I. Mordant Red 19		
	transfer dyes and all information to		Hispacrom Violet B	RBM	
1481	C.I. Mordant Violet 1	transfer to	C.I. Mordant Violet 5		
1586	C.I. Mordant Black 3	for read	Java Chrome Blue Black B	Vond	
1593	C.I. Mordant Black 17	for read	Java Chrome Blue Black BN... ..	Vond	
1708	C.I. Disperse Violet 8	transfer to	Java Chrome Blue Black R	Vond	
			Java Chrome Blue Black RN... ..	Vond	
			Diacelliton Fast Violet B	MCI	
			C.I. Disperse Violet 4		

VOLUME 2

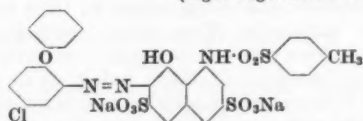
2037	C.I. Direct Orange 1	transfer to	Direct Fast Orange PRN	Vond	
2053	C.I. Direct Orange 43	in the heading for read	C.I. Direct Orange 31		
2054	delete C.I. Direct Orange 45		Stilbene		
	transfer dye and all information to		Disazo		
2174	C.I. Direct Blue 12	transfer to	C.I. Direct Orange 37		
2275	C.I. Direct Brown 31	transfer from	Trimaal Blue CVBN	Vond	
2285	C.I. Direct Brown 57		C.I. Direct Blue 151		
	under "The following brand is similar"	transfer to	Trifon Brown S, SP	Vond	
2286	C.I. Direct Brown 59	for read	"identical" to "similar" listing		
2303	delete C.I. Direct Brown 120		Direct Dark Brown NZ	Vond	
	transfer dyes and all information to		C.I. Direct Brown 190		
			Hispamin Brown BD	RBM	
			Hispamin Brown DB	RBM	
			C.I. Direct Brown 95		

VOLUME 2—continued

Page					
2350	C.I. Direct Black 74	transfer to	Diazol Light Grey 4B	Fran
			C.I. Direct Black 103 (new entry)	...	
2364	C.I. Sulphur Yellow 3	transfer to	Sulfer Yellow 2G	Vond
			C.I. Sulphur Yellow 6	...	
2371	C.I. Sulphur Red 1	transfer to	Sulfer Brown W...	Vond
			C.I. Sulphur Brown 56	...	
2373	C.I. Sulphur Red 6	for read	Sulfer Red Brown R	Vond
			Sulfer Red Brown RN	Vond
2386	C.I. Sulphur Green 3	transfer to	Sulfer Brilliant Green 5G	...	Vond
			C.I. Sulphur Green 7	...	
2396	C.I. Sulphur Brown 10	transfer to	Sulfer Brown B	Vond
			C.I. Sulphur Brown 8	...	
2397	C.I. Sulphur Brown 12	transfer to	Sulfer Brown BR	Vond
			C.I. Sulphur Brown 56	...	
2557	C.I. Vat Black 18	for read	Carbanthrene Grey MBM	...	NAC
			Carbanthrene Grey GFL	...	NAC
	under "The following brand is similar" delete		Carbanthrene Grey GFL	...	NAC
2615	C.I. Azoic Coupling Component 7	for read	Diathol AS-SW	MCI
			Diathol SW	MCI
2618	C.I. Azoic Coupling Component 17	for read	Diathol AS-BS	MCI
			Diathol BS	MCI
	C.I. Azoic Coupling Component 18	for read	Diathol AS-D	MCI
			Diathol D	MCI
2619	C.I. Azoic Coupling Component 20	for read	Diathol AS-OL	MCI
			Diathol OL	MCI
2835	C.I. Solvent Orange 7	transfer from	Sudan Scarlet 6G	G
			"identical" listing to "similar"	...	
2874	C.I. Solvent Blue 4	for read	Victoria Blue Base	Fran
			Victoria Blue B Base	Fran
2927	C.I. Developer 8	under Note for read	B.O.N.S.	...	
			B.O.N.A.	...	
2932	C.I. Reducing Agent 6	for read	Vacolite	S
			Vacolite	LBH

VOLUME 3

3107 add

18134 C.I. Acid Red 249 (new entry)
 (Light bright bluish red)
5-Chloro-2-phenoxyaniline → *N-p*-Tolylsulfonyl H acid

3646	under Aniline, 2,5-dimethoxy-	for read	35811
			35810

OBITUARY NOTICES

Peter Castle Floud, C.B.E.

The death of Mr. Floud on 22nd January 1960 at the early age of 48 is a great loss to all interested in the history of the English calico printing industry. Except for absence during the war he had held appointments on the staff of the Victoria and Albert Museum, becoming Keeper of the Department of Circulation in 1947. He had conducted widespread research into the history of the English calico printing industry and at the time of his death he was engaged both in preparing an exhibition illustrating the history of English printed textiles to be held at the Victoria and Albert Museum during the coming summer and in putting the finishing touches to a series of

papers for the *Journal*. It is hoped that we shall yet be able to publish these papers both for their own interest and value and as a memorial to the work of the foremost historian of the English calico printing industry.

Raymond W. Jacoby

We regret to report the death of Raymond W. Jacoby, a past president and 8th Olney Medallist of the A.A.T.C.C., on 14th December 1959, at the age of 70. Mr. Jacoby had occupied many official positions in the A.A.T.C.C., including membership of their *Colour Index* Editing Committee from its inception and after the dissolution of that committee he served on the *Colour Index* Supplement Editorial Committee until his death.

New Books and Publications

Symposium on Dyeing and Finishing of Textiles, Melbourne, 1959

Pp. 3 + 143. Melbourne University: Society of Dyers and Colourists of Australia. 1959. n.p.

This handsomely produced volume is the record of the first symposium to be held by one of our affiliated societies. It was held on 28th-30th May 1959 in the Chemical School, Melbourne University, and was opened by Mr. R. G. Casey, the Australian Minister for External Affairs and Minister in Charge of C.S.I.R.O. To have such a distinguished Australian Minister to open the symposium was both an honour for the Australian Society and a recognition of the status they have now achieved. The contents of this volume, which include Mr. Casey's address, the ten papers delivered at the symposium and the discussions on them, will further add to the prestige of our Australian colleagues. The papers themselves are dealt with in the Abstracts section of this issue.

C. O. CLARK

The Story of Chemical Industry in Basle

Basle: Ciba Ltd. Pp. 234. 1959.

Although this book claims to be no more than a portrayal of the genealogy and shape of chemical industry in Basle, its canvas is greatly wider. Necessarily concise, it gives a clear picture of cultural developments since the scholasticism of the late Middle Ages began to feel the impact of intellectualism based on a rational preoccupation with nature. If the theme seldom strays far from Basle, it is only because that city-canton was singularly well-blessed in possessing nearly all that was favourable to the evolution of technology. Basle has been a remarkable spiritual anchorage for the scholarly and the skilled oppressed by political strife. The foundation of its University and the introduction of printing marked the zenith of Basle's municipal development and the opening of a phase of history upon which this book is based. The two Ciba chemists who wrote the text,

Dr. George Leo Huber and Dr. Karl Menzi, deserve congratulation for a scholarly approach and a breadth of vision so often lacking in those who look back as well as forward. The text follows an orderly pattern: Basle in the setting of the late Middle Ages, the influence of Renaissance and Humanism, the accession of mechanistic thought, and the triumph of rationalism. Having laid the ground, the authors develop their principal theme by describing how and why the seeds of chemical industry germinated in such rich cultural soil leading to the wonderful harvest of today. Quite properly, the emphasis is on the many and diverse manufactured chemical products of Switzerland, but the authors are never restricted by frontiers and are generous in their tributes to other nationals. They have needed help, of course, from the scholars and institutions which are the strength of Basle today as in the past. That their source material is abundant and rich is clear from the innumerable illustrations in monochrome and colour depicting title pages, medieval manuscripts, historic documents, and so much more besides. The book is an elegant production. The format is what it should be and the typography and illustrations are excellent. It is not faultless, but such criticisms as can be made are of no great matter. The spelling has an American flavour for which the book is none the worse, but actual errors (such as "naphtalene" on page 97) are rare. Speaking of the Heumann synthesis of indigo (page 135), "alkali amide" should read "alkali hydroxide". The systematic name for Salvarsan (page 161) is not that of the chemist. Sir John Pettus is wrongly referred to (page 128) as Sir John Pettres, and it is misleading to say that Peter Griess was affiliated with Allsopp & Sons as a consultant (page 128) when he was actually employed as a chemist, which is quite different. These points in no way detract from an uncommonly attractive book.

W. H. CLIFFE

Handbuch des Chemikers**Band II****Physikalische Eigenschaften
anorganischer und organischer Verbindungen**

Edited by B. P. Nikolski. Pp. 818. Berlin: VEB Verlag Technik. 1957. Price, DM 42.00.

Such are the vagaries of international politics that the land of the famous Landolt-Börnstein tables now publishes a translation of the Russian *Spravochnik khimika*. The German version was prepared at the University of Halle under the direction of Dr. S. Brandt, the actual translators being G. and M. Frank.

A table of physical and thermodynamic properties of the chemical elements is followed by an account of the principles of German inorganic nomenclature. The important point is made that purely trivial names are quite permissible, but that names which embody scientific views of chemical constitution which have since been rejected are not to be allowed, and should disappear from the technical and patent literature. The table of physical properties of inorganic compounds covers 136 pp., but this is because of the large number of compounds (2,708), for the properties include only molecular weight, refractive index, density, melting and boiling points, and solubility.

The account of organic nomenclature has been rewritten by the German editors, and leans heavily on the Geneva system. The table of physical properties of organic compounds extends to nearly 500 pp. and 8,000 compounds with a formula index, but, again, few properties are included. Finally, separate tables are given for refractive index (in numerical order) of solids and liquids, and for the specific rotation of organic compounds.

C.J.W.H.

High Polymers**Volume XII****Analytical Chemistry of Polymers****Part I****Analysis of Monomers and Polymeric Materials
Plastics, Resins, Rubbers, Fibres**

Edited by Gordon M. Kline. 1959. Pp. xviii + 666. London and New York: Interscience Publishers. Price, 125s. 0d.

Part I of *Analytical Chemistry of Polymers* is primarily concerned with the analytical test methods used in relation to commercial monomers and polymers. Part 2, which is in preparation, will deal with molecular structure determination, chemical group analysis, and identification. Of the twenty chapters contained in Part I, each of which is allocated to one class of polymer or allied topic, all but one of the authors are associated with the American polymer industry. The greater part of the book is devoted to synthetics such as acrylic, alkyd, phenol, and epoxy resins, as well as silicone and vinyl polymers, but provision is made for natural resins, celluloses, proteins, and rubbers, together with chapters on drying-oils, ion-exchange resins, fibres, and plasticisers.

The primary aim of the book is to collect together some of the many and diverse procedures of high polymer analysis, with an emphasis upon

hitherto unpublished or little known tests and in many cases diagrams of apparatus, results, and characteristic spectra are presented. Although for the sake of completeness attention is drawn to standard and established tests this is deliberately brief but amply supported by references to the original literature. This paring of available information is also revealed by the somewhat brief introduction to each chapter and the generally condensed construction of many of the evaluation formulae which are presented.

One of the minor criticisms which may be levelled is that although generally speaking the information provided is well within the scope of the book there appears to be cases where the same information, on the face of it, might fit even better in Part 2. For instance, interesting chapters on polyamides, in which monomers are discussed mainly from the point of view of degradation products, and polyethylene contain quite detailed accounts on physical structure. The chapter on fibres is free from this criticism and, although mainly concerned with the synthetics, contents itself with straightforward analysis. At the same time comprehensive analytical procedural tables are included for up to twenty-three fibres occurring either singly or in binary mixtures. The chapter on drying-oils appears to be well covered, supported as it is with over two hundred references. In a book such as this it is not surprising, although perhaps a pity, that copolymers are not themselves provided with a separate chapter but are associated, where relevant, with chapters headed by the name of the parent homopolymer. A timely chapter on the epoxy resins should be welcomed, which for all its more recent development is given one of the longest chapters in the book.

The overall presentation is of the usual high standard of this series of monographs on High Polymers and because of the effort which has gone into its preparation the book is not too bulky to be carried around. It will presumably be not so much of interest to the more academic student as to the technological student and the practical technologist. It should therefore be a welcome addition to the laboratory bookshelf not only as another volume in this well known series but as a reference book of specific analytical procedures.

R. P. SHELDON

Tables of**Interatomic Distances and Configuration
in Molecules and Ions**

Edited by L. E. Sutton. Pp. 31 + 19 + 259 + 69 + 9. London: The Chemical Society (*Special Publication No. 11*). 1958. Price, 42s 0d. (\$6.00) (36s. 0d. to Fellows of the Chemical Society).

A collection of results from electron-diffraction studies on gases, made by Dr. P. W. Allen a decade ago, was the origin of the present far more comprehensive and elaborate work, which is a co-operative production by specialists in many fields. Its publication at a reasonable price has been facilitated by an advance purchase by the United

States Army, and the filing equipment was bought with a grant from Imperial Chemical Industries Ltd.

For the first time, a critical compilation has been made of all the quantitative results (published up to the end of 1955) of chemical significance relating to the shapes and sizes of molecules and ions in the gaseous and solid states. Data for about 2,000 substances, obtained mainly from measurements of diffraction and analyses of spectra of various types, are arranged, together with literature references, in inorganic and organic tables, which are self-indexing by empirical formula. A table of selected bond lengths gives values of interatomic distances which are deemed to correspond to chemical bonds and to be known to within ± 0.02 Å. The introductory sections describing the arrangement of the tables contain a useful account of error.

Unfortunately, relatively few of these results are of direct interest to the dyer and colourist, possibly because the dye and polymer molecules with which he is mainly concerned are too large and complex for such detailed numerical treatment. However, the tables do include such compounds as sodium hydroxymethanesulphonate, nitroanilines, *cis*- and *trans*-azobenzene (so presumably these two forms really do exist), indigo, thioindigo, anthraquinone, flavanthrone, etc. For indanthrone it is stated that the molecule is not planar, the two rings at each end being effectively planar and lying on parallel planes 0.27 Å apart, and that "the three central rings show a slight staggering of the atoms", which brings to mind an essential feature of our symposia. This is the sort of information on which any final theory of the perennial question of "colour and constitution" must one day be firmly based.

The Chemical Society and all concerned are to be congratulated on this valuable work. The scientific editor states in his preface: "This compilation has proved a very much bigger task than any of us had expected. We have all had to work under pressure; . . .". Several members of our own Society will appreciate to the full what he means!

C.J.W.H.

British Instruments

Directory and Buyers' Guide 1959

Scientific Instrument Manufacturers' Association.

Pp. 322 + 293. London: United Science Press Ltd. Price, 42s. 0d.

Although this lavish catalogue has been designed mainly for trade purposes, useful technical information is provided incidentally. The practical dyer may not find here the perfect answer to all his testing and control problems, but at least this guide may help in providing answers to the fair proportion of inquiries received by the Society that are concerned with instruments.

Section 1 gives information about twelve associations allied to the instrument industry, and an editorial surprise here is the word *lampblown*, which relates to glassware fashioned by manipulation in an oxy-gas flame. This is followed by lists of relevant British Standards, consultants, and

firms able to develop ideas and make prototypes. Section 5 (120 pp.) is a classified list of instruments and components with the firms which make them, and here one can see which "ometers" really do exist, though unfortunately no definitions are given: colorimetric analysers, fluorescent analysers, barkometers (for dogs or tanners?), blanchometers, choppers (offensive weapons?), colorimeters, colour comparators, print register controllers, glassmeters, illumination meters, light integrators, keratometers, lossmeters (to record thefts?), computer memories, textile permea(m)eters, sunshine recorders, fading (textiles) test equipment (but the well known manufacturers of fading lamps are not mentioned), wobblers.

Section 6 is, again, of wider interest, and is described as a "four-language glossary", but in fact it consists of three alphabetical lists, of French, German, and Spanish terms respectively, with English equivalents corresponding to the headings in Section 5. One would have thought it helpful to British firms to have included an alphabetical list of the English terms with their translations in the above languages; this could well be done in Section 5 with little additional effort or cost.

Sections 7-10 consist of a list of manufacturers with overseas agents, selected trade names, reference sheets, and display advertisements, respectively.

C.J.W.H.

Analytical Applications of Diaminoethanetetra-acetic Acid

By T. S. West and A. S. Sykes. Pp. 106. Poole: British Drug Houses Ltd. [1959.] Price, 4s. 6d.

This little booklet is a tribute to the versatility as an analytical reagent of the "title compound", more succinctly if less explicitly known by the initials EDTA, though unfortunately, from the point of view of readers of this *Journal*, most of the analyses described will be of greater interest to e.g. metallurgists than to textile chemists.

The first chapter (14 pp.) summarises the chemical and physicochemical aspects of the use of EDTA in analysis. It forms chelate complexes with nearly all metal ions, including some of the alkali metals, and is exceptional among complexing agents in reacting stoichiometrically and instantaneously. The useful information is given that the Complexones, the name being the registered trade-mark of the Uetikon Co. of Switzerland, are a group of polycarboxylic amino acids characterised by the group $N(CH_2\cdot COOH)_2$; this now well established offence to systematic chemical nomenclature was given to these compounds by Schwarzenbach in 1945.

The second chapter (22 pp.) is devoted to indicators for EDTA titrations, and these are nearly all colorants, ranging from murexide to the delightfully named di-SNADNS. It might have been useful to give *Colour Index* numbers in this chapter: at the end the authors do mention "British Colour Index No. 302", but they really

should have known that the definite article without nationality is adequate designation.

The next two chapters deal with physical methods of end-point detection and masking and demasking agents, the latter including formaldehyde and triethanolamine. Chapters on the determination of metals and anions are followed by one on the hardness of water, including methods for estimating total, calcium, and magnesium hardness together with a useful table showing the effects of foreign ions on hardness determinations.

EDTA is used in the analysis of several technical materials, including magnesium in leather, zinc in paints, zinc and sulphate in viscose-coagulating solutions, and xanthates. It is used also as a masking agent.

The final chapter gives formulae of eight analogous compounds, but among these only 1,2-diaminocyclohexane-*NN'*-tetra-acetic acid (DCTA) shows appreciable advantages over EDTA, and because of its superior complexing powers can be used to titrate even calcium in relatively acid solutions.

The booklet terminates with 468 references.

C.J.W.H.

The Textile Recorder Annual 1959-1960 Book of the Year

Manchester and London: Harlequin Press (1955)
Ltd. Pp. 154. 1959. Price, 30s. 0d.

This publication follows the usual pattern of very general surveys of developments in and the outlook for the various branches of the textile industry, illustrated by a few graphs and many pictures. Perhaps the most striking information to be gained from the article on textile finance is the extent to which many large firms, particularly those in the dyeing and finishing industry, have diversified their interests, partly as a protection against the vagaries of the textile industry, with the object of using both their financial resources and their scientific knowledge in new and expanding industries; these diverse interests include coffee houses, property, retail distribution, jet engines and nuclear engineering, chemical engineering, plastics, paving, etc.

Progress in bleaching, dyeing, and finishing is surveyed by A. J. Hall, in five pages, but since ten of his 35 references are to this *Journal*, and most of the others will have been covered in our abstracts, our readers should already be well acquainted with the information contained therein. Five pages also are devoted to new dyeing and finishing machinery, but although there have been improvements in design and control, few machines based on new principles have been brought out.

C.J.W.H.

A Catalogue of Shell Films in International Circulation

Pp. viii + 91. London: Shell Petroleum Co. Ltd. 1958. n.p.

A list of over 250 films available on loan free of charge. They may be obtained in either 35 or 16 mm. gauge but without exception must be projected in sound projectors at sound speed (24

pictures per sec.). Their length varies, the time taken for their showing being a few minutes for the shortest films to half an hour for the longest. Advice is given on how to select programmes for different audiences. A synopsis is given of each film and there is an alphabetical list of them. The subjects covered are most varied, from *Acid Treating through Cooks Kitchen, History of the Helicopter, New Detergents to Winter Moth*. It will be most useful to those arranging meetings for students, specialists or general audiences.

C. O. CLARK

Methods of Test for Textiles

Amendment No. 1

British Standards Institution. PD 3439. Amendment 1959 to B.S. Handbook No. 11: 1956. London. Pp. 9.

So many new and revised specifications for testing textile properties have been evolved since the 1956 edition of this handbook that it would be inappropriate to reproduce them as an amendment, but the subject of water repellency testing has been so controversial and is of such general interest that immediate action to publish new recommendations was thought necessary. The new procedure proposed by the Textile Institute entails stricter control of certain details in the Bundesmann test enabling it to be used for quality control testing within a laboratory, but variability between tests on different machines may still be great.

The amendment includes corrigenda to the existing text of the handbook, and a useful list of new and revised standard methods of test relating to textiles published since the 1956 edition.

C.J.W.H.

British Standard Method of Test for the Recovery of Fabrics from Creasing B.S. 3086 : 1959

British Standards Institution. Pp. 11. London. Price, 4s. 0d.

In general the Society is concerned more with the chemical (or physicochemical) changes undergone by textiles than with the details of their mechanical properties, but since the object of many chemical finishing processes is to produce a change in physical and dimensional properties, it is necessary to measure the latter in order to estimate the success of the chemical finishes. For this reason, the Society is vitally concerned with measuring the recovery of fabrics from creasing, and has been represented on the committee entrusted with preparing the present standard, which is based on Tentative Textile Standard No. 44 of the Textile Institute. The method is intended for dress and other apparel fabrics, but is unsuitable for very limp or very thick fabrics. A rectangular specimen is folded in half, maintained thus for a specified time under a specific load, and allowed to recover to some extent after removal of the load, when the angle between the arms of the specimen is measured. Suitable apparatus is described.

C.J.W.H.

**British Standard Method of Test for
Cotton Fibre Maturity**
(Estimation by Classification of Fibres swollen in
Sodium Hydroxide Solution)

B.S. 3085 : 1959

British Standards Institution. Pp. 8 + 1 plate.
London. Price, 3s. 0d.

The Society has been directly represented on the committee entrusted with the preparation of this British Standard, which is based on Tentative Textile Standard No. 47 of the Textile Institute. Mature cottons with thick walls often dye deeper in colour than immature cottons with thin walls. For the test, fibres are swollen with 18% sodium hydroxide solution, examined under the microscope, classified as normal, thin-walled, or dead, and counted. The percentages of the three classes of fibres are combined into a single index, the *maturity ratio*, which is directly proportional to the degree of wall thickening. The standard includes definitions, photomicrographs of typical fibres, and detailed instructions for carrying out the test. A single test is based on an examination of five mounted microscope slides, each containing about a hundred fibres.

C.J.W.H.

**Influence of Colorant Systems on Thermal
Protection**

By Alvin O. Ramsley. Pp. vi + 52. Natick, Mass.: Headquarters Quartermaster Research & Engineering Command, U.S. Army. *Textile Series Report No. 105*. 1959.

The present Parts III-V of this series describe laboratory studies on convective heat flow in fabrics exposed to high-intensity radiant energy, the rôle of direct transmission, and the influence of secondary layers respectively. Fabric assemblies have been exposed to intense radiant energy of short duration, and observations and conclusions are essentially empirical rather than theoretical.

Part III describes a procedure for analysing the shape of time-temperature curves in terms of modes of heat flow. The area under such curves can be greatly reduced by inclusion of an impermeable layer, e.g. regenerated cellulose film, within the assembly.

The contribution of simple conduction through spaced systems is less important than other methods of heat flow. To obtain high levels of protection with a khaki outer layer, direct transmission should be diminished by appropriate coloration of secondary layers (nylon taffeta dyed with 20% Disperse Fast Black BA, cotton sheeting dyed with 10% Vat Direct Black RB, and both fabrics pigmented with resin-bonded aluminium

flakes or by vacuum deposition of aluminium were tested).

The passage of hot volatile decomposition products appears to be one of the more important methods of heat flow.

C.J.W.H.

**Improved Inks for Letterpress Four-colour
Printing**

B.S. 3020 : 1959

British Standards Institution. Pp. 11 + 5 plates.
London. Price, 6s. 0d.

The Society was directly represented on the committee entrusted with the preparation of this British Standard, and is interested in the subject in three quite different ways: its general concern with technical aspects of colour and coloration, its concern with the accurate reproduction of coloured illustrations for papers in the *Journal*, and its interest in acceptance by advertisers of the use of standard coloured inks, which greatly affects the amount of work entailed in printing the monthly issues of the *Journal*.

A standard set of three-colour inks was devised in 1929 by organisations representing printers, printing-ink manufacturers, and process engravers, and in 1949 B.S. 1480 covered a set of four-colour inks as well. The new inks are better but more costly than the existing ones, and therefore the two British Standards will run concurrently for the present. The new inks have greater colour strength, and the magenta and the cyan are considerably brighter, resulting in purer secondary colours and reduced tendency to appear grey in lighter tones. They are sufficiently transparent to use in any necessary sequence. The technically undesirable "bronzey sheen" on certain of the inks has been reduced.

The standard specifies colour, colour strength, transparency, and light fastness (by reference to the Society's test B.S. 1006) for a set of yellow, magenta, cyan, and black inks. Prints made with the inks are included using a step-wedge block instead of progressive proofs. Appendixes A and B give spectrophotometric curves and a zinc oxide reduction test for colour strength respectively. A useful and perhaps unusual feature is the discussion in Appendix C of the background to the standard: until it is possible to produce commercially prints having a controlled ink film thickness, and the surface to be printed can be accurately standardised, empirical specification in terms of master standard inks must be retained in preference to specification of colour in terms of instrument readings on prints.

C.J.W.H.

New Books received

A.S.T.M. Standards on Textile Materials (with related information). Philadelphia: American Society for Testing Materials. October 1959. Pp. xxii + 902. \$8.50.

Chemical Analysis. Volume XI. *X-Ray Spectrochemical Analysis*. L. S. BIRKS. New York and London: Interscience Publishers. Pp. xii + 137. 1959. 44s. 0d.

The Journal 1958-1959. Bradford: The Bradford Textile Society. Pp. 120 + 14 illustrations. 1959. 12s. 6d.

The Story of Chemical Industry in Basle. Basle: Ciba Ltd. Pp. 234. 1959.

Knitterechtmachen in Rezeptform. Hochveredlung von Textilien. RUDOLF GÜNTHER. München-Gladbach: Lapp-Verlag. Pp. 242. 1959. DM 9.85.

Rezeptbuch für Faserstoff-Laboratorien. Mikroskopische und chemische Textiluntersuchungen. P.-A. KOCH. Berlin-Wilmersdorf: Springer-Verlag. Pp. viii + 239. 1960. DM 31.50.

- Vat Dyeing of Cotton Piece.** Blackley, Manchester: Imperial Chemical Industries Ltd. 2nd edition 1959. Pp. viii + 107 + 10 plates.
- High Polymers. Volume XII. Analytical Chemistry of Polymers. Part I—Analysis of Monomers and Polymeric Materials (Plastics, Resins, Rubbers, Fibres).** GORDON M. KLINE (editor). New York and London: Interscience Publishers. Pp. xviii + 666. 1959. 125s. 0d.
- Removing Spots and Stains.** I. MELLAN and E. MELLAN. New York: The Chemical Publishing Co. Inc. Pp. 95. 1959. \$4.50.
- Physical Methods of Investigating Textiles.** R. MEREDITH and J. W. S. HEARLE (editors). New York: Textile Book Publishers Inc., a division of Interscience Publishers Inc. (and London). Pp. ix + 411 + 13 half-tones. 1959. 88s. 0d. (\$13.00).

- Man-made Textile Encyclopedia.** J. J. PRESS (editor). New York: Textile Book Publishers Inc., a division of Interscience Publishers Inc. (and London). Pp. xiv + 913. 1959. 200s. 0d. (\$27.50).
- Die Farbe Band 7.** 1958 (Bound Volume). MANFRED RICHTER (editor). Göttingen: Musterschmidt-Verlag. Pp. ii + 308.
- Advances in Spectroscopy. Volume I.** H. W. THOMPSON (editor). New York and London: Interscience Publishers. Pp. x + 363 + 21 half-tones. 1959. 85s. 0d. (\$12.50).
- Technique of Organic Chemistry. Volume I. Physical Methods of Organic Chemistry. Part I.** ARNOLD WEISSBERGER (editor). New York and London: Interscience Publishers. 3rd revised and augmented edition. 1959. Pp. xii + 918. 184s. 0d.

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., 68, 23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index

I—PLANT; MACHINERY; BUILDINGS

PATENTS

Mounting of Working or Support Rollers

Zimmer's Erben BP 822,833
Rollers not provided with axles are prevented from bending by being supported throughout their whole length solely by bearing boxes which partly embrace each roller. C.O.C.

J-boxes for Treating Yarns

British Cotton and Wool Dyers' Asscn. BP 818,333
The J-box is divided into compartments by vertical partitions. Inclined glass plates, spaced apart, are supported by the partitions and the side walls to form the front and rear walls of the compartments, through which air can enter in order to come into contact with the yarn in the box. C.O.C.

Continuous Rope or Open-width Washing Machine

Deering Milliken Research Corp. BP 817,384
A perforated cylinder constructed to provide an internal flow-path for the cloth is mounted horizontally in a tank. It has inwardly directed longitudinal baffles and oscillates about its axis through an arc of < 180°. The level of the liquor in the tank is such that the cylinder is at least partly below it. This enables continuous operation to be combined with agitative action on the cloth and liquor. C.O.C.

Drum Washing or Dyeing Machines

Cherry Tree Manufacturing Co. BP 819,251

Tenter

Proctor & Schwartz USP 2,894,334
Describes an arrangement of the air distribution nozzles which leads to greater drying efficiency. C.O.C.

Apparatus for Flaming the Surface of Polyethylene Film

Plax BP 827,195

Surface Treatment of Organic Thermoplastic Films to Render them Receptive to Printing Ink

A. Sestini BP 827,429
Machine in which the films are passed between electrodes fed by high frequency current of high voltage. Printing inks adhere tenaciously and without any spreading to the treated films. C.O.C.

Printing or Decorating Ceramics, Glass, Plastics, etc.

Murray Curvex Printing BP 827,984
Machine for automatically operating the processes described in BP 735,637 and 736,312 (J.S.D.C., 71 (1955) 689 and 739). C.O.C.

Dyeing Cloth Continuously in Rope Form (VIII p. 254)

II—WATER AND EFFLUENTS

PATENTS

Clarifying an Aqueous Suint Bath containing Wool Grease and reusing the Bath for Wool Scouring
U.S. Secretary of Agriculture USP 2,897,043

Purification of Emulsified Aqueous Effluents

Minister of Supply BP 819,440
Oily contaminants present in emulsified form in aqueous effluents are removed by adding a sulphate of cerium, lanthanum or neodymium. The flocculating agent is recovered by adding a little dilute sulphuric acid to the flocculated layer when separation into two layers occurs. The upper layer contains the oil contaminants and the lower, aqueous layer the acidified flocculating agent which is recovered and reused after neutralising the excess acid present. C.O.C.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Important Factors to consider when selecting Water-soluble Gums

C. M. Ferri
Amer. Dyestuff Rep., 48 (14) (13 July 1959) 32-4

New Sizing and Scouring Auxiliaries

P. Ya Mukhanov *Tekstil. prom.*, 19 (Aug 1959) 76-79
Use of a dark coloured cellulose sulphite extract, a by-product in the production of alcohol, as a water soluble sizing agent is described. The sizing properties compare favourably with starch, yielding well penetrated soft handling yarns. The preparation at the sizing plant is shown diagrammatically, consisting of dissolving, neutralising from pH 5-6, and setting. Recipes for sizing union yarns are given. A sulphonated fatty acid, a by-product from margarine manufacture, is recommended as a wetting and emulsifying agent. G.J.K.

A Mild-cure Catalyst

J. B. Irvine, J. K. Simons, and J. H. Davids
Amer. Dyestuff Rep., 48 (12) (15 June 1959) 37-42, 50
A mixture of aluminium chloride hexahydrate and magnesium chloride hexahydrate is well suited for use where curing at 250-265°F. is desired, e.g. where gentle curing of low strength fabrics is required. C.O.C.

Fluoro Chemicals

E. J. Grajeck and W. H. Petersen
Amer. Dyestuff Rep., 48 (12) (29 June 1959) 37-9
A brief historical review of the fluorocarbons and their uses. C.O.C.

Latices in the Textile Industry

L. L. Shailer *Can. Text. J.*, 77 (1) (8 Jan 1960) 45-8
A general account with no details or recipes of the present use of latices in the manufacture of bonded fibre

fabrics, dimensional stabilisation, back coating of carpets and other pile fabrics, laminated fabrics, decorative and functional finishes, pigment binding, wear resistance, heat sealing, and improving fastness to rubbing. C.O.C.

Organic Insecticides and Fungicides. Synthesis of Some Aromatic Esters of Halogenated Phenoxyacetic Acids

N. N. Mel'nikov and I. L. Vladimirova

Zhur. obshch. khim., 29 (Nov 1959) 3587-3589

Several esters of 2,4-dichlorophenoxy-, 2,4,5-trichlorophenoxy- and pentachlorophenoxyacetic acids were prepared from acid chlorides and phenols. The pentachlorophenyl ester of 2,4,5-trichlorophenoxyacetic acid is an effective fungicide. L.S.L.

PATENTS

Rosin Size

Hercules Powder Co.

BP 828,202

A paste rosin size of improved stability against crystallisation is obtained by treating rosin with 0.5-4.0% of its weight of HCHO in presence of an acid catalyst and then saponifying with an alkali metal hydroxide or carbonate. C.O.C.

Coal-acid Compounds for Sizing Nylon Yarn

Dow Chemical Co.

BP 819,192

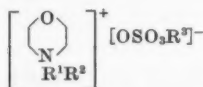
The yarn is treated with a plasticised mixture of the aromatic acid compounds obtained from the oxidation of coal. The plasticiser is preferably water, the coal-acid compounds being best applied from aqueous solution. The sized yarns stand well up to weaving and the size is completely removed during normal scouring. C.O.C.

Antistatic Finish for Polyacrylonitrile Fibres

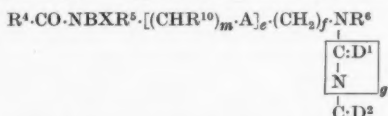
Chemstrand Corp.

BP 824,168

An antistatic lubricant for polyacrylonitrile fibres consists of (1) 20-50% by weight of a non-ionic surface-active, partial ester of an aliphatic carboxylic ester of a polyhydric alcohol (acid of 10-20 C, alcohol of 2-8 C); (2) 15-35% of a non-ionic surface-active polyether obtained from 150-250 mol. ethylene oxide and 1 mol. water-insoluble hydroxy fatty acid; (3) 10-40% of a compound of formula—



(R¹ = Alk of < 5 C; R² = Alk of > 10 C; R³ = Alk of < 5 C); and (4) 5-25% of a compound of formula—



(R⁴ and R⁹ = satd. Alk of > 5 C; R⁴, R⁶, R⁷ and R⁸ each = H, Alk or hydroxyalkyl of < 5 C and R⁴ and R⁷ may = residue from an acid amide from an acid and a polyamine; D¹ and D² = O, S or amido; g = 0-3; A = O, S, imino, alkyl or alkylol (> 5 C) subst. N, methyl or hydroxy-subst. alkyl; f and j = 1-6; e and k = 0-6, m and t = 1-6; R¹⁰ and R¹¹ = H or CH₃; B = Alk or cationic H; X = Hal or the anion corresponding to B), e.g. 36% sorbitan monopalmitate, 24% castor oil-ethylene oxide condensate, 20% N-cetyl, N-ethyl morpholinium ethosulphate and 20% [β-(N-acetoxy, N-stearoyl)ethyl-β-hydroxyethyl]urea. C.O.C.

Derivatives of Aminotriazine- or Urea-formaldehyde Condensates as Antistatic Agents

Ciba

BP 818,844

Derivatives of aminotriazine- or urea-formaldehyde condensates with alcohols of 1-4 C, capable of being hardened and which contain basic N atoms, at least one free or etherified methyl group and polyglycol ether chains or several hydroxethyl groups but no epoxy group, when applied to textile fibres and hardened impart an excellent antistatic finish. C.O.C.

Sulphonated Pentahalogeno Compounds as Antistatic Agents

Dow Chemical Co.

BP 818,337

Sulphonated pentahalogeno compounds, e.g. the quaternary salt from pentachlorobenzene sulphonic acid and dodecyl trimethyl ammonium chloride, are excellent antistatic agents particularly for acrylic fibres. C.O.C.

Water-soluble Vinyltoluene Copolymer Sulphonates—Textile Assistants

Dow Chemical Co.

BP 823,113

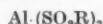
Non-crosslinked water-soluble resin sulphonates are obtained by mixing SO₃ with a liquid solution of a solid thermoplastic copolymer of 55-90% by wt. of *ar*-vinyltoluene and 45-10% of a lower alkyl acrylate or methacrylate at > 40°C., the reactants being dissolved in a chlorinated aliphatic hydrocarbon inert to SO₃. Their aqueous solutions decrease in viscosity on prolonged standing and/or heating. Thus they can be used as thickeners for dye pastes which when applied to fabric and boiled decrease in viscosity so that the water-soluble material is readily washed out. C.O.C.

Organic Aluminium Sulphinates—Water-repellent Agents for Cellulosic Products

Monsanto Chemical Co

BP 819,181

Compounds of formula—



(R = Alk or aralkyl of 4-18 C), e.g. aluminium trioctyl sulphinate, are used to impart water-repency to cellulosic textiles, paper, etc. Their manufacture is described. C.O.C.

Siloxane Water-repellent Finish for Fibrous Materials

Union Carbide Corp.

USP 2,895,853

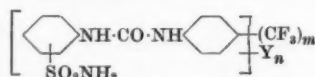
Products suitable for producing a water-repellent finish on textiles, paper, etc. are obtained by cohydrolysing dimethyldichlorosilane (3-50 parts) with dichlorosilane (1). C.O.C.

Mothproofing Agent for use in Neutral to Weakly Acid Dyebaths

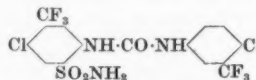
Gy

BP 828,231

Compounds of formula—



(Y = Hal; m = 0-2; n = 0-5; m + n = > 1) e.g.—



obtained by treating 2-amino-4-trifluoromethyl-5-chlorobenzene sulphonic acid amide with 3-trifluoromethyl-4-chlorophenyl isocyanate, applied from a weakly acid dye bath, impart good protection to wool against attack by clothes moths and carpet beetles. C.O.C.

Trifluoroacetic Anhydride for Partial Acetylation of Cotton Cellulose (VI p. 250)

Use of Sulphuryl-8 in Sulphur Dyeing (VIII p. 252)

Tetrahydropyrimidinone Derivatives for Non-chlorine Retentive, Crease-shedding Cotton Fabrics (X p. 256)

Synthetic Resins for Chlorine-fast "Wash-and-Wear" Finishes (X p. 256)

Chlorine-resistant Blends of Triazone and Urea Derivatives for Crease-shedding Cotton Fabrics (X p. 256)

Polarographic Analysis of Driers (XIV p. 260)

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Azo Compounds

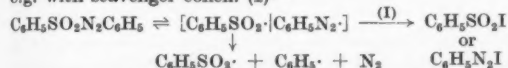
A. J. Rosenthal and C. G. Overberger

XXXII—Kinetics of Thermal Decomposition of Phenylphenylsulphonyl Diimide

J. Amer. Chem. Soc., 82 (5 Jan 1960) 108-117

Phenylphenylsulphonyl diimide was prepared from a mixture of benzene diazonium chloride in nitrous acid,

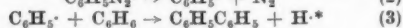
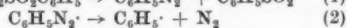
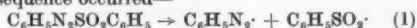
free aqueous HCl and sodium benzenesulphonate in water at 5°C. Thermal decomposition of this product was studied in benzene and alkylbenzene solvents by nitrogen evolution and by a colorimetric procedure based on formation of benzenazo- β -naphthol. An acidic product autocatalysed the reaction, the autocatalysis being inhibited by addition of CaO. In benzene there was a twofold increase in decomposition rate over the range 60–70°C. and fourfold from 70–80°C. In toluene, xylene, and ethyl benzene at 70°C. and low concn., rates were similar to those in benzene but at higher concn. were concn. dependent. The addition of oxygen, iodine, trinitrobenzene, chloranil, styrene, vinyl acetate or acrylonitrile further accelerated the decomposition of diimide. Mechanism of decomposition in the presence of such radical scavengers may be a bimolecular reaction between the scavenger and diimide, a radical induced first order decomposition or a capture of restricted (or "caged") radicals by a reactive scavenger, e.g. with scavenger concn. (I)—



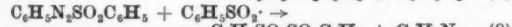
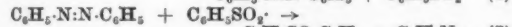
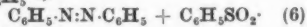
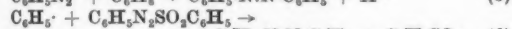
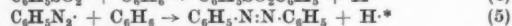
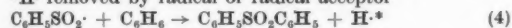
XXXIII—Products of Thermal Decomposition of Phenylphenylsulphonyl Diimide

Ibid., 117–119

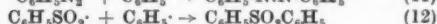
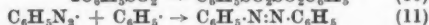
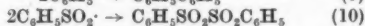
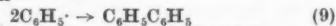
The decomposition of phenylphenylsulphonyl diimide was studied in benzene and *p*-xylene. The products were found to be consistent with a mechanism involving cleavage of the starting material into phenylazo and phenylsulphonyl radicals. These radicals could initiate the polymerisation of styrene, methyl methacrylate, vinyl acetate, and acrylonitrile. A polystyrene was also obtained containing azo and sulphone groups. In benzene the following sequence occurred—



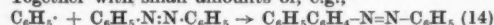
*H· removed by radical or radical acceptor



Radical combination—



Together with small amounts of, e.g.,



F.J.

Binary Systems of Benzidine with Organic Acids

A. P. Arestenko and A. G. Bergman

Zhur. obshch. khim., 29 (May 1959) 1744–1749

Phase diagrams of the binary system benzidine–organic acid (acetic, propionic, *n*-butyric, isobutyric, isovaleric, *n*-caprylic, stearic, benzoic, and salicylic) have been studied. Compound formation with a stoichiometric ratio of 1 benzidine to 1 acid molecule occurs with all except salicylic (1:2) and benzoic acid (1:1 and 1:3).

G.J.K.

Recent Advances in Dye Technology

J. H. Anderson

Dyeing and Finishing Symposium, Melbourne, 1959, pp. 127–143

Discusses recent progress in both the manufacture and the application of dyes.

C.O.C.

Relationship of Colour to Constitution of Chemical Compounds

D. A. Pospelkov

Trudy Odessk. Sel'skokhoz. Inst. 9 (1957) 71–82

Chem. Abs., 53 (25 Oct 1959) 18573

A critical review (59 references). Chromophores are considered as individual atoms with an incomplete electron shell rather than as coordinatively unsaturated atoms. Such an approach provides a general explanation

of colour phenomena in organic coordination compounds; it is also applicable to inorganic compounds, particularly metal carbonyls, but not to inorganic complex salts.

C.O.C.

Relationship between Constitution and Fastness Properties of Dyes. II—Fastness on Wool of Monoazo Dyes derived from Tolyazonaphthalene

B. I. Stepanov and M. V. Zakharova

Izvest. Vysshikh Ucheb. Zavedenii, Tekhnol.

Tekstil. Prom. (2) (1959) 117–124

Chem. Abs., 53 (25 Oct 1959) 19393

Introduction of ether groups into dyes derived from tolylazonaphthalene and phenylazonaphthalene generally improves their fastness (on wool) to wet processing and carbonising. This is especially the case with alkoxy groups, the effect increasing with increasing number of C atoms in the alkyl radical of the ether group. Ether groups, especially alkoxy groups, also improve fastness to rubbing. Fastness is usually increased by one point.

C.O.C.

A Century of Synthetic Dyes for Cellulosic Fibres

S. Coffey

Chem. and Ind., (6) (Feb 1960) 132

An outline of developments leading to the introduction of reactive dyes for cellulose. Formulae for a Procion Yellow, Red, and Blue are given.

E.S.

Studies in Indigoid Dyes. XXII—Thioindigoid Dyes derived from Dibenzofuran-2-sulphonic acid

P. C. Dutta and B. C. Dash

J. Indian Chem. Soc., 36 (Sept 1959) 609–612

Preparation of 2,3-dibenzofurano-3'-hydroxy-1'-thiophene from dibenzofuran-2-sulphonic acid, and its condensations with various *O*-diketones (acenaphthenequinone, phenanthrenequinone, aceanthraquinone, β -naphthothiofuran-1,2-dione, 9,10-phenanthrathiophene-2,3-dione, glyoxal sodium bisulphite, and 2,3-dibenzofuranthiophene-2',3'-dione), are described. These thioindigoid dyes are insol. in alkaline hydrosulphite, so their depth of colour is recorded from their absorption max. in xylene soln. The bathochromic effect is in the order—phenanthrene indigos > ethylene > acenaphthylene > indol > aceanthrylene; the longer the conjugation between the two chromophores >C=O, the deeper is the colour.

H.H.H.

Thermal Stabilities and I.R. Spectra of some Solid Metal Salt Stabilised Diazonium Salts

A. F. Gremillion, H. B. Jonassen, and R. J. O'Connor

J. Amer. Chem. Soc., 81 (5 Dec 1959) 6134–6138

The stabilities of solid salts formed from the chlorides of Fe²⁺, Zn²⁺, Cd²⁺, Sn²⁺, Sb³⁺, Hg²⁺, Bi³⁺ and *p*-dimethylaminobenzenediazonium chloride have been studied by measuring the rate of nitrogen evolution at 98°C. and the I.R. spectra of the solids have been recorded. Correlation between the nitrogen evolution rate and the electronic configurations of the metal ions and the electro-negativities of the metal atoms has been found. Possible modes of interaction between the metal ion and the diazonium ion are discussed. Water in the unit cell makes the solid diazonium salt less stable.

F.J.

Dissociation of Malachite Green (C.I. Basic Green 4)

K. Shekhter, A. V. Savitskii, and I. I. Moiseev

Zhur. obshch. khim., 29 (Nov 1959) 3625–3627

In an aqueous solution of dioxan (2.9%) with a phosphate buffer at pH 5.29 (when the carbinol base should be fully dissociated (*sic*)) Malachite Green (5×10^{-6} M.) has molar extinction coefficient at 620 m μ . of 7.70×10^4 , and at 562 m μ . a value of 2.17×10^4 . The pK varies from 7.18 at 15°C. to 6.64 at 35°C. corresponding to $\Delta H = 10.6$ kcal./mole and $\Delta S = 4.18$ e.u., the latter varying with the ionic strength of the solution. Calculations from other data that the activation heat and entropy of dissociation are $\Delta H^* = 25$ kcal./mole and $\Delta S^* = 6.2$ e.u., lead to the conclusion that the activated complex is a solvated polarised molecule or an ion pair.

L.S.L.

Kinetics of the Fading of Chrysoidine under Ultrasonics

S. Prakash and S. Prakash

J. Indian Chem. Soc., 36 (Sept 1959) 601–604

The fading at concn. of 0.016, 0.014, 0.012, and 0.028 g. per l. of chrysoidine by ultrasonic waves from a Mullard's generator with barium titanate crystal of frequency 1 Mc./sec. and energy input 225 w. is unimol. with average velocity const. 0.221, 0.238, 0.243, and 0.285 respectively.

Although H_2O_2 is produced in small concn. when ultrasonic waves are passed through water, the fading does not appear to be due to it, but to the rupture of the mol. of chrysoidine by the high energy of cavitation of the waves.

H.H.H.

Relation of Dye Structure to Properties of Disperse Dyes

V. S. Salvin and R. A. Walker

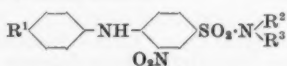
I—Anthraquinone Blues

Amer. Dyestuff Rep., 48 (13 July 1959) 35-43

Dyeing and fastness properties on cellulose acetate and polyester fibre of condensation products of various arylamines with dinitro-chrysazin and -anthrarufin are described. The products are of good fastness to burnt gas fumes. A hydrophilic group, such as m - CH_2OH , in the arylamine used, leads to enhanced dyeing properties for cellulose acetate, whereas the more hydrophobic products exhaust better on to polyester fibre. Some mixtures of isomers give increased dyebath stability and build-up of dye on fibre.

II—Diphenylamine Yellows

A series of dyes of formula—

*Ibid.*, 43-47

($R^1 = H, OAlk, NH_2$ or $NH-CO-CH_3$; $R^2, R^3 = H, Alk, hydroxyalkyl$, or phenyl) was prepared, and dyeing and fastness properties on cellulose acetates and Dacron were examined. The simplest members have good dyeing properties but low wet fastness on cellulose diacetate and triacetate. Increase in mol. wt. leads in general to improved wet fastness with slower rate of dyeing, and the product in which $R^1, R^2 = H$, and $R^3 = phenyl$ is a commercially available dye of good light- and wet-fastness on these fibres.

E.S.

Phthalocyanine Crystal Spectra

L. E. Lyons, J. R. Walsh, and J. W. White

J.C.S., (Jan 1960) 167-175

Quant. predictions of the spectra of metal-free phthalocyanine crystals, based on the theory of crystal splitting of their intense absorption bands (cf. Craig and Walsh, *J.C.S.*, (1958) 1613; Bern and Bradburn, *Proc. Camb. Phil. Soc.*, 39 (1943) 104), are compared with the experimental polarised spectra of single crystals now reported. The theory is found to be deficient only insofar as it relies upon experimentally determined intensities and bands which are not of negligible width as required by the theory. The assignment of each pair of upper states near 15,000 cm^{-1} and 28,000 cm^{-1} to B_{1u} and B_{2u} symmetry in D_{4h} (E_u in D_{4h}) seems none the less to be reasonably certain for metal-free phthalocyanine and related cpd. An appendix gives the method of treating a doubly degenerate level in D_{4h} .

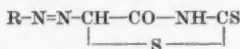
H.H.H.

Synthesis and Transformations of Thiazolidine Derivatives

A. P. Grishchuk and S. N. Baranov

Zhur. obshch. khim., 29 (May 1959) 1665-1667

Seven azorhodanines (AZ) of type—



($R = e.g. HOOCCH_2H_3$) have been prepared in good yields by coupling diazonium salts of some amines with rhodanine in ammoniacal soln. AZ are intensely coloured, acidic, and give characteristic reactions with Ag, Cu, and Hg salts.

G.J.K.

Merocyanines derived from Oxazolone

P. B. Tripathy and M. K. Rout

J. Indian Chem. Soc., 36 (Sept 1959) 625-631

Preparations of merocyanines are described from oxazolone (I) and quinaldine, lepidine, 2-methylbenzothiazole, 4-phenyl-2-methylthiazole, α -picoline, and benzo (f)-quinoline-2 respectively, and the effect of the oxazolone nucleus on their absorption is determined. The relative acidity of I compared with thiohydantoin (II) and rhodanine (III) is assessed from the deviation data of the appropriate merocyanines; the deviations are 12 $m\mu$, 67.5 $m\mu$, and 27 $m\mu$ respectively, and indicate (cf.

Brooker, *J. Amer. Chem. Soc.*, 73 (1951) 5332) that I is more acidic than III, which in turn is more acidic than II. This data is supported by resonance interpretations. Experimental data also establish the theoretical prediction of enhanced acidity for the oxazolone nucleus substituted by a nitro-group.

H.H.H.

Cyanine Dyes containing Unsaturated Groups. Dimethinmerocyanines Derivatives of Rhodanine containing Unsaturated Substituents in the Benzothiazole nucleus

M. A. Al'perovich, I. K. Ushenko, L. N. Tyurina, and M. K. Grechko

Zhur. obshch. khim., 29 (Nov 1959) 3606-3612

A number of cyanines containing styryl and ω -phenylbutadiene substituents in the benzylthiazol nucleus have been obtained. Introduction of unsaturated groups shifts the absorption maximum towards the end of the longer wavelength part of the spectrum. Absorption maxima of dimethinmerocyanines in various solvents are given.

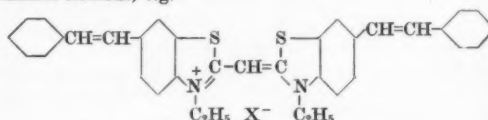
L.S.L.

Monomethincyanines and Styrene Dyes containing Styryl and β -Phenylbutadiene Radicals, i.e. Benzthiazole Nuclei

I. K. Ushenko and S. E. Gornostaeva

Zhur. obshch. khim., 29 (Nov 1959) 3807-3814

Reacting diazotised 2-methylmercapto 6-aminobenzothiazole with cinnamic p -methoxycinnamic and styrylacrylic acids under Meerwein reaction conditions produced three new bases each containing an unsaturated substituent in position 6. When treated with an alkylating compound quaternary salts were formed. Quaternary salts with active methyl groups were condensed in absolute alcohol in presence of triethanolamine with a quaternary salt of 2-methyl mercaptobenzothiazole to yield monomethincyanines having unsaturated groups in the benzthiazol nucleus, e.g.—



Introduction of an unsaturated radical into a 6-6' position in monomethincyanines produces a bathochromic effect to the extent of 60 $m\mu$.

L.S.L.

Photographic Properties of Some Symmetrical Carbocyanine Dyes having Different Alkyl Groups on the Nitrogen of the Heterocyclic Groups

I. I. Levkoev and E. B. Lifshits

Zhur. Nauch. i Priklad. Fot. i Kinematografi., 3 (1958) 419-426*Chem. Abs.*, 53 (25 Oct 1959) 18703

Contrary to the literature methylates and ethylates of a series of dyes (with indolenine, thiazoline, benzimidazole and thiadiazole [1,3,4] groups) have much the same sensitising action, but with thia-, oxa-, and quino-(2)-carbocyanine dyes, the NN' -dimethyl derivatives are significantly less effective than the ethyl analogues.

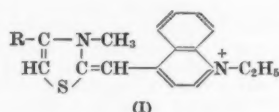
C.O.C.

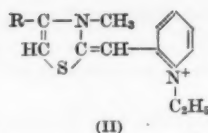
Unsymmetrical Methin Cyanines derived from Quinoline and Pyridine

B. Das and M. K. Rout

J. Indian Chem. Soc., 36 (Sept 1959) 640-642

Two series (I and II) of unsymmetrical methin cyanines are described: (I) formed by reaction of quinoline ethiodide with methiodides of the following thiazoles: 2-methyl-4-phenyl-, 2-methyl-4- p -bromophenyl-, 2-methyl-4- p -ethoxyphenyl-, 2-methyl-benzo-, and 1,2 dimethyl-benzimidazole; (II) by substituting 2-iodopyridine ethiodide for quinoline ethiodide in the first reaction. The absorption maxima are measured to evaluate the relative order of basicity of the variable basic nuclei used, and the highest shift towards the shorter wavelength region was achieved by incorporation of the benzimidazole nucleus.





(II)

H.H.H.

Characterisation of Vegetable Dyes by Paper Chromatography

R. R. Paris and R. Rousselet

Ann. pharm. franc., 16 (1958) 747-756*Chem. Abs.*, 53 (25 Oct 1959) 19393

R_f values and recommended solvents are given for: anthocyanins, Alizarin (C.I. 75330), sulphonated alizarin, Campeachy Wood (C.I. Natural Black 1), Brasilin (C.I. Natural Red 24), Acacia Cacho (C.I. Natural Brown 3), Caramel (C.I. Natural Brown 10), Carotene (C.I. Natural Yellow 26), Chicory, Chlorophyll (C.I. Natural Green 3), Cochineal (C.I. Natural Red 4), Curcuma (C.I. Natural Yellow 3), extract of *Rhamnus insectoria*, Indigo (C.I. Natural Blue 1), Indigo Carmine (C.I. Natural Blue 2), Myrtillin (from *Vaccinium myrtillus*), Alkanna (C.I. Natural Red 20), Orseille (C.I. Natural Red 28), Purpurin (C.I. 75410), Quercitron (C.I. Natural Yellow 10), Riboflavin, Rocou (C.I. Natural Orange 4), Saffron (C.I. Natural Yellow 6), resin from *Calamus draco* (cf. C.I. Natural Red 3), and Xanthophyll. C.O.C.

Fungus Pigments. VIII—Constitution of Cinnabarin and Cinnabarinic Acid

J. Gripenberg

Acta Chem. Scand., 12 (1958) 603-6110 (in English)*Chem. Abs.*, 53 (10 Nov 1959) 20064

Evidence which shows that cinnabarin is 2-amino-9-(hydroxymethyl)phenoxazin-3-one-1-carboxylic acid and that cinnabarinic acid is 2-aminophenoxazin-3-one-1,9-dicarboxylic acid. C.O.C.

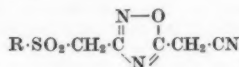
PATENTS

Colour Couplers for producing Magenta Images

Gevaert Photo-Producten

BP 817,286

Compounds of formula—



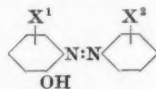
(R = Alk or subst. or unsubst. Ar, e.g. R = β -naphthyl), used as photographic colour couplers in presence of a primary aromatic amino developing agent, yield magenta images. C.O.C.

Yellow to Orange Disperse Dyes

FH

BP 826,959

Yellow to orange dyeings of good fastness properties are obtained on polyester fibres by use of an aqueous suspension of a dye of formula—



(X¹ = Cl or Alk or alkoxy of 1-4 C; X² = H, Cl, Alk or alkoxy of 1-4 C, trifluoromethyl or an aldehyde group), e.g. 4'-methyl-5-chloro-2-hydroxy-1,1'-azobenzene dyes polyester fibre greenish yellow. C.O.C.

Acid Salts of Triarylmethane Basic Dyes for use in Spirit Reproducing Transfer Materials

Caribonum

BP 828,394

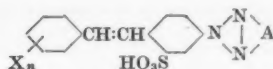
Mixing an aqueous solution of a triarylmethane basic dye with an aqueous solution of a triarylmethane acid dye, preferably in stoichiometric proportions, precipitates a dye which is completely insoluble in water and only very slightly soluble in perspiration. They quickly dissolve in methylated spirit without loss of colour. Thus the dye obtained from C.I. Basic Violet 3 and C.I. Acid Violet 17 is readily incorporated into a normal spirit reproducing "carbon" paper wax and oil base and used to form a coating which should it soil the hands is readily washed off. C.O.C.

Fluorescent Brightening Agents

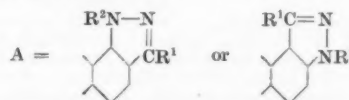
HW

BP 828,329

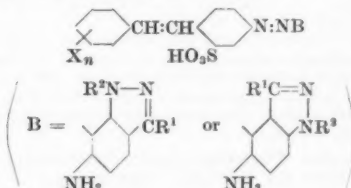
Compounds of formula—



(X = H or a non-chromophoric and non-auxochromic group; n = 1-5;



(R¹ = H or hydrocarbon; R² = H, hydrocarbon, hydroxy-alkyl or polyethanoxy group) e.g. 2-(4''-styryl-3'-sulphophenyl)(indazolo-4',5'-4,5)-1,2,3-triazole, are obtained by oxidising a dye of formula—



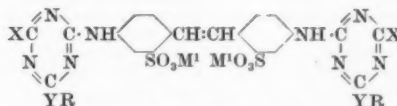
They are fluorescent brightening agents for cellulosic materials and have good fastness to bleaching agents both in solution and on the fibre. C.O.C.

Fluorescent Brightening Agents for Natural and Polyamide Fibres

S

BP 827,567

Compounds of formula—



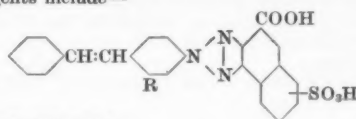
(X = Hal; Y = O or S; R = Alk of 1-4 C, alkenyl of 1-4 C, alkoxyalkyl (alkoxy of 1-4 C, Alk of 1-4 C), or aralkyl containing 1-2 aliphatic C; M⁺ = H or alkali metal), obtained by reacting, in any desired order, 1 mol. of a 4,4'-diaminostilbene-2,2'-disulphonate, 2 mol. of a cyanuric halide and 2 mol. of a compound of formula—R-Y-M² (M² = H or cation) in water at 0-20°C. in a first stage and 20-50°C. in a second stage. They are fluorescent brightening agents which exhaust on to polyamide fibres from neutral or weakly acid baths at 70-100°C. They have very good fastness to light, heat setting, washing, perspiration, hypochlorite, and peroxide. C.O.C.

Fluorescent Brightening Agents for use in making Polyamides and Polyurethanes

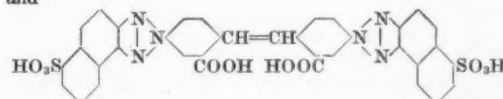
FBY

BP 827,745

Fluorescent brightening agents containing groups capable of combining chemically with the polyamides or polyurethanes under the conditions prevailing during polymerisation are added to the monomers. Examples of such agents include—

(R = CN, SO₂CH₃)

and



C.O.C.

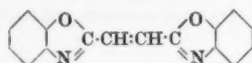
Fluorescent Brightening Agents for Polyester Fibres

Ciba

BP 827,992

Excellent results are obtained by use in aqueous medium at > 75°C. of fluorescent brightening agents free from water-solubilising groups and containing at least one

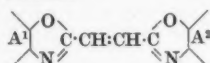
heterocyclic ring fused on to a benzene ring and finally treating the fibres with dry heat at $> 100^{\circ}\text{C}$. Thus Terylene fabric is padded with a dispersion containing per 1,000 parts of water 0.6 part of



and 1.2 part of ethylene oxide-*p*-*t*-octylphenol condensate (8 mol.:1 mol.), dried at 60°C . for 30 min. and then baked at 130°C . for 10 min. This yields the same effect as applying the same amount of the agent in a boiling bath.

BP 828,545

Compounds of formula—



(A^1 and A^2 = benzene residues which may be substituted by Alk, alkoxy, alkylamine, acylamino or Hal), e.g. *αβ*-di-[5-methylbenzoxazolyl-(2)]-ethylene, are excellent fluorescent brightening agents for polyester fibres. They are applicable from dye, bleaching, scouring, sizing, and resin-finishing baths. C.O.C.

Water-soluble Phthalocyaninesulphonamides—

Reactive Dyes for Cellulose, Nylon, etc.

ICI

BP 826,689

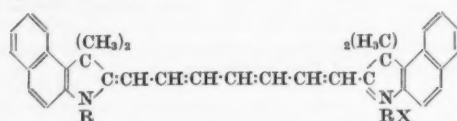
Derivatives of copper phthalocyanine (C.I. 74160) (I) which contain, attached to the benzene rings, at least one SO_3H group, and at least one group $-\text{SO}_2\text{R}$ ($\text{R} = -\text{NH}-\text{CH}_2-\text{CH}_2\text{Cl}$, $-\text{NH}-\text{CH}_2-\text{CH}_2\text{Br}$, or $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{OSO}_3\text{H}$, or derivatives in which the CH_2 groups may carry CH_3 or C_2H_5 as substituents), preferably in the 3'-positions, give blues of good wet fastness on cellulose, when applied by processes involving a treatment with an acid-binding agent. They may also be applied to wool, silk, leather, polyamides, and polyacrylonitriles. Thus I is heated at $135-140^{\circ}\text{C}$. with chlorosulphonic acid, cooled, drowned in ice and water, and the filtered and washed sulphonylchloride is stirred with aq. β -chloroethylamine. The product contains ca. 1.8 β -chloroethyl sulphamyl groups and 2.2 SO_3H groups per mol., the substituents being in the 3'-positions. It may be applied to viscose yarn from a dyebath containing NaCl; after 30 min. at 90°C . aq. NaOH is added and treatment continued for 1 hr. It is then washed successively in water, 4% aq. NaHCO_3 , and boiling 0.3% aq. soap to give bright greenish-blue very fast to washing. E.S.

Tricarbocyanine Infrared-absorbing Dyes

Eastman Kodak Co.

USP 2,895,955

Dyes of formula—



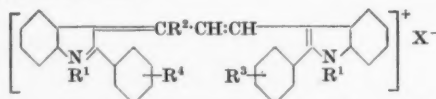
(R = subst. or unsubst. Alk of $< 5 \text{ C}$; X = acid radical) obtained by condensing a suitable cyclammonium quaternary salt with glutonic-aldehyde dianilide hydrochloride in presence of an anhydride, have excellent infrared absorbing properties. C.O.C.

Cyanine Dyes

Agfa

BP 825,965

Dyes of formula—



(R^1 = Alk; R^2 and R^4 each = H, Alk, alkoxy or Hal; R^3 = H, Alk, cycloalkyl, thienyl or $\text{R}^2\text{C}_6\text{H}_4$; X = anion) e.g. bis-(1-methyl-2-phenyl-indolyl-3-trimethincyanine bromide, are deeper coloured than bis-indole-cyanines and can be made more deeply coloured by suitable substitution in the 2-position of the indole ring and in the trimethin chain. They are particularly suitable for sensitising direct positive silver halide emulsions. C.O.C.

Carbon Black (C.I. Pigment Black 6 and 7)

Phillips Petroleum Co.

USP 2,895,805

Method and apparatus for controlling the temperature of a stream of hydrocarbon charging stock when making Carbon Black. C.O.C.

Carbon Black (C.I. Pigment Black 6 and 7)

Columbian Carbon Co.

USP 2,895,804

Method of obtaining a pigment of desirable fineness and hysteresis properties by dispersing hydrocarbons in a stream of hot gas. C.O.C.

Lead Silicophosphate Pigments

Hoyt Metal Co. of Great Britain

BP 827,634

A pigment consisting of PbO , P_2O_5 and SiO_2 in physico-chemical combination there being 2.8 mol. PbO per mol. P_2O_5 and 0.75–7.5 mol. SiO_2 per mol. PbO yields paints which do not change in viscosity during storage and which have marked resistance to blistering. They may be made by any method which brings the components together in the necessary intimate contact, e.g. an aqueous solution of phosphoric acid or a phosphate is added to an aqueous slurry of PbO and SiO_2 with vigorous agitation. The product is filtered off and calcined at $700-800^{\circ}\text{C}$. for 1–3 hr. C.O.C.

Titanium Dioxide (C.I. Pigment White 6) for Pigmenting Synthetic Polymer Films or Sheets

National Lead Co.

BP 824,509

TiO_2 coated with 0.25–10.0% by weight of a hydrous oxide of Al, Ti, Si or Zr and 0.2–5.0% of a compound of formula $\text{R}^1\text{-C}(\text{OH})\text{R}^2\text{-COOR}^3$ (R^1 = Alk or Ar; R^2 = H, Alk or Ar; R^3 = H, NH_4 , alkali metal, alkaline earth metal, Alk or Ar), e.g. lactic acid, is readily dispersible in organic solvents to yield dispersions very suitable for incorporation in synthetic polymers to be used for forming films or sheets. C.O.C.

Photosensitive System consisting of a Heteropolytungstic Acid and an Oxidisable Organic Substance

L. Chalkley

USP 2,895,892

A mixture of a heteropolytungstic acid and an oxidisable organic substance becomes coloured on exposure to light. When this colour is caused only by the reduced heteropolytungstic acid, i.e. the oxidised organic substance is colourless, then the colour fades again in the dark, i.e. the process is phototropic. The fading, which takes place in the light as well as the dark, opposes the photochemical process and on prolonged exposure to light of constant intensity a constant colour is obtained that no longer varies with time of exposure and depends only on the intensity of the light. Thus photographic material based on such a system is self-restoring and can be used repeatedly, e.g. as reusable printing out papers. Window curtains sensitised with such a system adjust themselves to the intensity of illumination to which they are exposed, e.g. when intensity is low such curtains have little colour and admit much light, but when the sun shines on them they darken and reduce transmission of light and glare into the room. There are many other fields of use of the process, thus if the oxidisable substance is the leuco base of a triphenylmethane or xanthene dye then instead of the simple dye which is fugitive to light being formed there results the much more stable heteropolytungstate toner of the dye. Suitable acids are silicotungstic acid $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, borotungstic acid $\text{H}_4\text{BW}_{12}\text{O}_{40}$, luteophosphotungstic acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$, and 12-series phosphotungstic acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$. C.O.C.

Exposure Studies of Organic Pigments in Paint Systems (V p. 249)

Hue of some Direct Dyes on Cotton (VIII p. 251)

Coupling Weakly Reactive Diazo Compounds with Azotols on Cotton and Viscose Rayon (II) (VIII p. 251)

Trihydroxyphenols as Oxidation Bases in Hair Dyeing (VIII p. 254)

Chromatography of Flavonoid Pigments (XIV p. 261)

Separation and Identification of Artificial Colours authorised by the Italian Hygiene and Sanitation Commission 23rd Dec. 1957 for use as Food Dyes (XIV p. 261)

Synthetic Food Colours. I—Characteristics and Properties of the Water-soluble Dyes approved for use in Spain (XIV p. 261)

V—PAINTS; ENAMELS; INKS

Paint Vehicles. Part IV—Micro-rheology: Theory Classifications, Calculations

L. Dintenfuss

J. Oil Col. Chem. Assoc., 43 (Jan 1960) 46-53

A short synopsis of the micro-rheological theory developed by the author is given, and some limitations of the treatment are suggested; thus, the quantitative treatment applies only to Newtonian liquids, or to dilatant liquids at very low rates of shear where the dilatancy is negligible and may be neglected. Rheological classification of paint vehicles is suggested; the described types include Newtonian, dilatant, and thixotropic systems and some combinations of these systems. A table of physical constants of some solvents is given to facilitate calculations. C.O.C.

Baked Polyurea Coatings

G. A. Hudson, J. C. Hixenbaugh, E. R. Wells, J. H. Saunders, and E. E. Hardy

Ind. Eng. Chem., 51 (Nov 1959) 1383

A brief outline of structure and properties. J.W.D.

Isocyanate Coatings Based on Castor Oil

G. C. Toone and G. S. Wooster

Ind. Eng. Chem., 51 (Nov 1959) 1384-1385

An account of the properties of films from systems consisting of a diisocyanate and castor oil transesterified with eight different polyols. J.W.D.

Urethane Coatings from Castor Polyols

T. C. Patton and H. M. Metz

Ind. Eng. Chem., 51 (Nov 1959) 1383-1384

A review of formulations and properties. J.W.D.

Stable Pigmented (Polyurethane) Coating Systems

R. A. Bieneman, E. J. Baldin, and M. K. Markoff

Ind. Eng. Chem., 51 (Nov 1959) 1387-1388

Polyurethane prepolymer systems that are normally stable frequently become unstable when pigmented; the primary cause is adsorbed moisture and other reactive impurities present in the pigments. Fair but not complete success has been attained in meeting these difficulties by reacting the impurities with isocyanate, by slurry grinding the pigment in a ball mill before adding the prepolymer. J.W.D.

Polyether Polyols in Urethane Coatings

A. Damusis, J. M. McClellan, and K. C. Frisch

Ind. Eng. Chem., 51 (Nov 1959) 1386-1387

Summary of the preparation and properties of coatings in which polyether polyols were used as—components of isocyanate-terminated intermediates, components of hydroxyl-terminated urethane intermediates, chain extenders for the above intermediates, and curing or cross-linking agents for isocyanate-terminated intermediates. J.W.D.

Statistical Studies on One-package Polyurethane Surface Coatings

S. N. Glasbrenner, B. Golding, and L. C. Case

Ind. Eng. Chem., 51 (Nov 1959) 1382-1383

Films given by an air-moisture cured system decreased in hardness with increasing addition of polymeric diol (this also improved the shelf-life of the finish) and increased with further excess of isocyanate. With isocyanate-adduct systems film hardness increased with lower mol. wt. of the triol and with lower triol-to-isocyanate ratios. In general film hardness varied inversely with the mean mol. wt. of the chains between branch points. With the moisture-cured system gelation was caused (under circumstances that should not have permitted it to occur) by side-reactions involving impurities such as moisture. J.W.D.

Reactions of Isocyanates with Drying Oils

G. Wilson and J. M. Stanton

Ind. Eng. Chem., 51 (Nov 1959) 1385

The reaction products of glycerol, pentaerythritol, or methyl glucoside with linseed or soyabean oils (either alkali refined or pre-bodied) may be further reacted with tolylene diisocyanate. Paints prepared from these media have been tested and found to be similar to those based on alkyds—inferior in some respects, superior in others. J.W.D.

New Pigment-mixture Diagram and Colour System

E. Friel

J. Opt. Soc. Amer., 49 (Dec 1959) 1159-1168

A diagram has been developed which summarises information about colour-mixture relationships among pigments, these relationships being expressed in terms of linear relationship among the points allotted to the pigments in the diagram. C.O.C.

Exposure Studies of Organic Pigments in Paint Systems

V. C. Vesce

Off. Dig. Fed. Paint Varn. Prod. Cl., 31 (419) (Dec 1959, Part 2) 5-143

Tables are given of the results of exposing 77 organic pigments in several systems, the resultant colour changes being reported in objective units of change. C.O.C.

PATENTS

Non-smudging Copying Ink Composition

Creed & Co

BP 819,319

The composition comprises a concentrated viscous solution of a black dye paste in an oily solvent and a wet press transfer medium dispersed in the dye paste. This transfer medium is a water soluble salt of a metal capable of reacting with a reagent to form a highly coloured compound in a wet press copy, e.g. iron sulphate and tannic acid. The ink must be free from particulate colorant. A suitable black dye paste is C.I. Pigment Black 18. C.O.C.

Coating Compositions

ICI

BP 826,009

Sprayable coating compositions comprise polymethyl methacrylate mol.wt. 60,000-100,000 (1-5 parts by weight), vinyl chloride/vinyl acetate resin (1), plasticiser (0-30% on wt. of methacrylate and resin) and a solvent of b.p. 130-250°C. They show increased gloss retention, durability, cold check resistance, petrol resistance, and adhesion. Their use also results in reduction in flocculation of some pigments, particularly Carbon Black (C.I. Pigment Black 6 and 7) compared with conventional methacrylate compositions. C.O.C.

Polarographic Analysis of Driers (XIV p. 260)

VI—FIBRES; YARNS; FABRICS

The Medieval Cloth Trade at Rouen

H. Wescher

Ciba Review, 12 (135) (Dec 1959) 7-9

A brief account of the history of the cloth trade at Rouen from the first records of dyeing and fulling being carried out there in 1199 to its decline at the end of the 17th century. C.O.C.

The "Rouennerie" Trade and its Entrepreneurs

H. Wescher

Ciba Review, 12 (135) (Dec 1959) 14-20

An account of the Rouen cotton cloth trade in the eighteenth century, mention being made of Fontenay's backing of Deseroizille's experiments in chlorine bleaching in 1787 and his opening of a very successful Turkey red dyehouse in 1792. C.O.C.

John Holker, a Promoter of the French Textile Industry

H. Wescher

Ciba Review, 12 (135) (Dec 1959) 10-13

An account of the career of John Holker of Stretford, who after serving in the Jacobite Manchester regiment in 1745 and later in the French army, established the cotton velvet industry in France, including dyeing and finishing. He was so successful in developing the French textile industry that he was subsequently appointed Inspector-General of Factories. C.O.C.

Influence of Surfactants on Physical Properties of Fibres

K. Fujii, T. Kamijo, and A. Nakatsugawa

J. Soc. Textile Cellulose Ind. Japan, 15 (Nov 1959) 906-910

Torsional rigidity, compressional elasticity, frictional coefficient and softness are studied experimentally. With wool and nylon there is no relation between the above properties. The properties of wool after treatment with various surface-active agents are influenced considerably. L.P.

Density of Packing of Macromolecules in Various Types of Cellulose

V. I. Sharkov and V. P. Levanova

Doklady Akad. Nauk S.S.S.R., 130 (1 Jan 1960) 109-110

The true specific gravity of various celluloses was measured by suspending dry samples in carbon tetrachloride at different temperatures. The samples were

then subjected to hydrolysis (10% H_2SO_4 at 100°C.) and alcoholysis (absolute ethyl alcohol containing 10% H_2SO_4 at 100°C.). New specific gravities were measured and plotted against the loss in weight of the samples. Cotton, ramie, wood pulp, and viscose were investigated. The results indicate that the original density and behaviour during hydrolysis and alcoholysis varied considerably depending on the source of the sample. L.S.L.

The Effect of Ionising Radiations on Cellulose

R. Imamura and H. Mizukami

J. Soc. Textile Cellulose Ind. Japan,
15 (Nov 1959) 931-938

Irradiation of cotton linters and high alpha sulphite pulp by X-rays causes degradation, shown by the decrease in the degree of polymerisation and the intrinsic viscosity. Thermal neutron and γ radiation cause a similar effect. The atmosphere in which the cellulose is stored after irradiation has considerable influence on the rate and extent of degradation. Thus, no change in the intrinsic viscosity is observed when wood cellulose (previously irradiated) is kept in N_2 or oxygen-free water vapour but gradual decrease is otherwise observed, oxygen-saturated water vapour being less effective than dry oxygen. Photomicrographs of the pulp before and after irradiation are given, together with ultraviolet and infrared spectra. L.P.

Relation between Dye Absorption and Cotton Fibre Properties at Equilibrium

P. N. Pal and K. M. Estere

Text. Research J., 29 (Oct 1959) 811-815

The relation was studied for nine cotton samples representing a large range of fibre properties, using both mercerised and unmercerised samples. For the American Upland type cotton a linear relationship was found to exist between maturity and dye absorption at equilibrium, and a relationship was also found between the Micronaire and dye absorption at equilibrium. S.B.D.

Partly Carboxymethylated Cotton as an Intermediate for Further Chemical Modification

R. M. Reinhardt, J. D. Reid, T. W. Fenner, and R. Y. Mayne

Text. Research J., 29 (Oct 1959) 802-810

Partly carboxymethylated cottons prepared by treating cotton with chloroacetic acid and caustic soda soln. retain the fibrous nature of cotton and in addition to immediate textile usage, are capable of further chemical modifications via the hydroxyl and carboxyl groups. Amongst the modifications discussed are salt formation, reactions for the introduction of cyanoethyl, carboxyethyl, and graft polyester groups, reactions with epoxy and aziridiny compounds, and oxidation. S.B.D.

Trifluoroacetic Anhydride for Partial Acetylation of Cotton Cellulose

C. Hamalainen, R. H. Wade, and M. D. Cruz

Text. Research J., 29 (Oct 1959) 821-826

Trifluoroacetic anhydride has been found to be an effective esterification promoter in preparing experimental quantities of partial cellulose acetates in which the fibrous structure of the cotton is retained. In this reaction the anhydride acts as an impellent and no additional catalyst is required. Effect of time, temperature, and molar ratio of the components in the reaction system have been studied. The optimum conditions are mild with no great degradative effects. Cotton yarns have been reacted, and the composition and physical characteristics of the modified yarns determined. S.B.D.

The Dynamics of Textile Materials. V—The Viscoelasticity of Viscose Rayon in Water at Various Temperatures and Extensions

K. Shirakashi, N. Oguchi, and H. Kaneko

J. Soc. Textile Cellulose Ind. Japan,
15 (Nov 1959) 868-872

The dynamic tensile Young's modulus and internal viscosity are measured by the free vibrational method (period 4-6 sec., maximum amplitude 1.5%). The viscoelasticities are linear at low extensions but non-linear at high extensions. The non-linear viscoelasticity can be analysed by the differential equation applied in an earlier paper, derived by treating it as arising from the breaking and re-forming of H-bonds. At low extensions the dynamic viscosity decreases with increasing temperature (25-50°C.) but does not change between 50-100°C. The dynamic modulus is not temperature dependent but the

dynamic viscosity is remarkably so and also increases with stretching. L.P.

Plasticity of Wool—V

K. J. Whiteley and J. B. Speakman

Text. Research J., 30 (Jan 1960) 46-50

Differences of substance among various wools play an important part in determining their suitability for use in manufacturing different types of fabric, and the quality in wool cannot be assessed by measuring only the dimensional characteristics of the fibres. S.B.D.

Stress-strain Curves of Soda-treated Wool Fibre

G. Satlow

Text. Research J., 29 (Oct 1959) 841-843

Rabbit Fibres. XXX—Fundamental Observation of Shrinkage. Advancing of Fibres between Two Layers of Various Substances

S. Ikeda

J. Soc. Textile Cellulose Ind. Japan,
15 (Dec 1959) 992-1000

Movements of untreated and carotated Angora rabbit fibres have been observed when rubbed between two substances (glass, Cellophane, rubber, paper, human skin, and felt) and passed through a slit. Fibres advance in the direction of their roots, the degree of advancement of free fibre probably being dependent upon the distribution of the coefficients of friction of anti- and pro-scale. F.J.

Moisture Sorption of the Silk of *Bombyx mori* in Relation to the Proportion and Chemical Composition of the Crystalline and Amorphous Phases

F. Lucas and S. G. Smith

J. Textile Inst., 50 (Dec 1959) T 695-T 700

Work which indicates that approximately 30% of the water sorbed at 65% R.H. is held by the crystalline phase, probably on the surface of the crystallites. This value for the availability of the reactive groups in the crystalline phase is confirmed by calculations based on the degree to which the aliphatic hydroxyl groups of fibroin can be methylated and tosylated. C.O.C.

Delustring of Artificial Fibres

P. I. Novoderezhkin

Tekhnol. tekstil. prom., No. 4 (11) (1959) 32-38

Dependence of lustre on the TiO_2 content, the nature of the surface, and the twist of yarns is treated theoretically, with special reference to the refractive index, acetate rayon being the fibre used. G.J.K.

Amidoximation of Partially Cyanoethylated Polyvinyl Alcohol Fibres

H. Itō

J. Soc. Textile Cellulose Ind. Japan,
15 (Dec 1959) 964-971

Amidoximation of partially cyanoethylated polyvinyl alcohol fibres in aqueous hydroxylamine hydrochloride containing 20% Na_2SO_4 at 100°C. and pH 7-9, gave fibres having improved elastic recovery at low elongations and higher affinity for acid, basic, vat, and disperse dyes. In formalisation of the treated fibres for shrink-resisting, the concentration of sulphuric acid used may be reduced to 10%. These fibres also show improved elastic recovery. F.J.

Studies of Japanese Paper Yarn. XXI, XXII—Limit of Yarn Twist

K. Yamada

J. Soc. Textile Cellulose Ind. Japan,
15 (Nov 1959) 887-896

Determination of the maximum twist possible by twisting (with a heavy traveller) a staple fibre yarn which is 50% saturated with water. When the twist tension is small, the yarn is doubly twisted but this is not so for large tensions. The limiting shrinkage due to twist y is proportional to the thickness of the yarn if the twist tension t and the moisture regain are constant; $y = at + b$. The limiting count N is proportional to the thinness of the yarn similarly, $N = At + B$. When the paper yarn begins to be doubly twisted there is a linear relation between twist tension, shrinkage, and count. The relation between twist tension and the limiting twist angle θ is given by

$$\frac{\epsilon_s}{100} = \left(\frac{1}{\cos \theta} \right) \left\{ 1 - \left(\frac{y}{100} \right) \right\} - 1$$

where ϵ_s = strain at fibre breakage. The relation between twist tension and the limiting twist angle by double twisting is $\tan \theta = Ct + p$ where C and p are constants. L.P.

PATENTS

Biological Water-retting of Flax

National Research Development Corpn. BP 825,704
A process enabling a series of rets to be carried out without need either to dispose of any retting effluent or to add any neutralising chemicals and with the acidity of the retting liquor controlled at that pH which results in the quickest retting consistent with a high yield of good quality fibre. C.O.C.

Bulky Resin-spun Rayon Yarn

American Viscose Corpn. USP 2,895,287
Water-resistant crimped yarn is produced by adding a suitable linear polymer, e.g. polyacrylamide, poly(ureido-alkyl vinyl ether), and poly(vinylalkyl alkylene urea) to viscose, producing yarn from the mixture, highly twisting the yarn and then treating it with formaldehyde and curing. C.O.C.

Bulky Mass-coloured Rayon

American Viscose Corpn. USP 2,895,288
Mass-coloured rayon yarn is supertwisted, impregnated with hot formalin in presence of a mildly acidic catalyst, dried, baked, and detwisted. The resultant yarn is very fluffy and crimped and remains so when immersed in water. The process is much quicker and more effective than it is when applied to non-pigmented yarn. C.O.C.

Foamed Polyurethane Yarns

W. Simon BP 825,838
Yarns formed partly or wholly of foamed polyurethane, e.g. by being cut from sheets, have open pores. Because of this they readily allow diffusion into the surrounding air. They can replace wool for many purposes. C.O.C.

Fluorescent Brightening Agents for use in making Polyamides and Polyurethanes (IV p. 247)

Fibres containing Active Methylene Groups and a New Dyeing Process for them (VIII p. 252)

History of the Development of Bonded Fibre Fabrics at Minnesota Mining & Mfg. Co. and their Dyeing (VIII p. 254)

Decorative Fabrics from Fibrous Glass—Coronizing Process and Coro-Dyed Yarns (X p. 257)

Cross-linking Cellulosic Materials by Irradiation (XI p. 259)

Stability to Laundering of Fabrics made from Cellulosic Fibres (XIV p. 260)

VII—DESIZING; SCOURING; CARBONISING; BLEACHING

Removal of Metal Ions from Cotton Fabrics

AATCC Rhode Island Sect.
Amer. Dyestuff Rep., 48 (26) (28 Dec 1959) 27-36
Chelating agents are effective in removing cations from cotton. All the agents studied were more effective at low pH and the organic ones were more effective at high temperatures. Sodium tetrakisphosphate has its optimum effect at room temperature and is at that temperature the most effective chelating agent of those studied. Ethylene diamine tetraacetic acid was the most effective of the organic agents studied, all of which had their optimum effect at high temperatures, at which temperatures they are more effective than the inorganic agents. C.O.C.

Clarifying an Aqueous Suint Bath containing Wool Grease and reusing the Bath for Wool Scouring (II p. 243)

The "Rouennerie" Trade and its Entrepreneurs (VI p. 249)

Production of Yarns for the Knitwear Industry (VIII p. 252)

Stability to Laundering of Fabrics made from Cellulosic Fibres (XIV p. 260)

VIII—DYEING

Turkey Red Dyeing in Rouen

H. Wescher *Ciba Review* 12 (135) (Dec 1959) 21-6
An account of the development of Turkey red dyeing in Rouen from the middle of the eighteenth century to the peak of its prosperity round about 1817. C.O.C.

Dyeing Properties of Azo Acid Dyes—IV

T. Iijima and M. Sekido

J. Soc. Textile Cellulose Ind. Japan, 15 (Nov 1959) 911-916

The adsorption by 6-nylon in neutral and alkaline solution of azo acid dyes based on α -naphthylamine \rightarrow β -naphthol is measured. The equilibrium adsorption at pH values greater than the isoelectric point is relatively high, e.g. naphthionic acid \rightarrow β -naphthol, 2.2×10^{-3} mmole/g. of fibre at pH 10. However, the adsorption is linearly dependent on the amino end-group content, even at pH 10. Linear extrapolation gives the adsorption of dye at zero amino end-group as 2.5×10^{-3} mmole/g. of fibre, which is equal to the adsorption of the parent dye. One explanation is that non-polar forces contribute to the affinity of these dyes but most of the adsorption at high pH values arises from the salt link between the dye anion and basic sites in the fibre. L.P.

Dyeing Under Reduced Pressure

N. D. Iljaschuk *Textil Praxis*, 14 (Dec 1959) 1267-1269

Describes the dyeing of textiles under partial vacuum (residual pressure 1-4 mm. Hg). A typical dyeing assembly is shown diagrammatically. Advantages claimed include shorter dyeing time, saving of steam, dyes, and auxiliaries. L.A.T.

Hue of Some Direct Dyes on Cotton

T. Urahata and Y. Ikeda

Kogyo Kagaku Zasshi, 61 (1958) 194-7
Chem. Abs., 53 (10 Nov 1959) 20809

Dyeings on cotton of Azo Blue (C.I. Direct Violet 28), Benzo Azurine G (C.I. Direct Blue 8), Sirius Violet 2B (C.I. Direct Violet 51), Brilliant Blue 5R, Oxamine Sky Blue 6B, Direct Blue 2B (C.I. Direct Blue 6), Oxamine Sky Blue 5B, Benzo New Blue 5B (C.I. Direct Blue 25), Brilliant Blue G, Sirius Supra Blue BRR (C.I. Direct Blue 71), Sirius Supra Blue G (C.I. Direct Blue 78), Diamine Fast Yellow A (C.I. Direct Yellow II), and Chrysamine G (C.I. Direct Yellow 1) were examined by reflective spectrophotometry to determine the change of chromaticity point with concentration in the C.I.E. chromaticity diagram. Relationship between luminosity and stimulus purity was also investigated. Most blue dyes showed increasing stimulus purity with increase of dye concentration up to a specific maximum followed by decrease. Rough linearity was observed between stimulus purity and luminosity at low concentrations. Dyes containing many sulphonic acid groups remain monomolecular even in high concentration whereas those with few such groups do not. C.O.C.

Physical State of Direct Dyes in Viscose and its Influence on Lightfastness

L. Weissbein and G. E. Coven

I—Examination of the Physical State of Direct Dyes in Viscose

Text. Research J., 30 (Jan 1960) 58-62
The use of ultra thin films of dyed viscose as primary specimens in an electron microscope enabled presence or absence of aggregates to be detected. Of two direct dyes dyed under the same conditions one was plainly aggregated and the other, having considerably poorer lightfastness, was unaggregated at a resolution limit of 30 μ .

II—Relation Between the Physical State of Direct Dyes in Viscose and Lightfastness

Ibid., 62-66
The methods of Part I were extended to several direct dyes of diverse chemical structure. Only two dyes showed no aggregates at the resolution limit of 30 μ , and these were considerably less fast to light than the others. S.B.D.

Coupling Weakly Reactive Diazo Compounds with Azotols on Cotton and Viscose Rayon (II)

R. M. Shchegoleva and F. I. Sadov

Tekstil. prom., 19 (Aug 1959) 37-39
Coupling of Diazo Blue O with Azotols on cotton and viscose rayon is investigated by establishing the e.m.f.-time dependence at the surface of the fabric. Coupling proceeded faster on viscose rayon than on cotton, the most active Azotol being PA, the least active MNA. Optimum pH range is 8.5-9.7. Experimental details of the e.m.f. determinations are given and the results fully tabulated. G.J.K.

Use of Sulphuryl-8 in Sulphur Dyeing

A. M. Sporkin and M. R. Tsimelev

Tekstil. prom., 19 (Aug 1959) 80
Dyeing sized fabric with sulphur dyes is improved by use of Sulphuryl-8 (2-ethyl-hexanol-sulphone ester) as a wetting agent in the dyebath. G.J.K.

Dyeing with Sulphur Dyes in Presence of Sulphur and Sodium Hydroxide

M. Rusanovschi and A. Friedman

Ind. textilă (Bucharest), 10 (1959) 111-2
Chem. Abs., 53 (10 Nov 1959) 20809
In dyeing with sulphur dyes Na_2S can be replaced advantageously by S_8 powder dissolved in boiling aq. NaOH. C.O.C.

Observations on Sulphur Dyeing Staple Rayon Fabrics Sized with Cellulose Ether

G. I. Yakimov and A. Z. Chernomordik

Tekstil. prom., 19 (12) (Dec 1959) 67-69
When desizing and dyeing in the same bath, it was observed that with certain sulphur dyes (brown and black) reaction occurred between the leuco form of the dye and the cellulose ether size (Preparation KMTS). The product of this reaction was insoluble in water and caustic soda and only partially soluble in sodium sulphide. The product was formed very rapidly and precipitated on the fabric causing a stiff and unpleasant handle. Importance of thorough desizing prior to dyeing, especially if a continuous dyeing method is to be used, is stressed. L.S.L.

Thermodynamic Study of the Vat Dyeing of Cellulose

P. V. Moryganov and M. I. Ortym

Izvest. Vysshikh Ucheb. Zavedenii, Tekhnol. Tekstil. Prom. (2) (1959) 125-133
Chem. Abs., 53 (25 Oct 1959) 19395

The levelling properties of some surfactants and solvents is in the following order—poly(vinylpyrrolidinone) > OP-10 > Cellosolve > pyridine > triethanolamine. The degree of affinity of vat dyes is comparable with that of direct dyes and decreases with increase in temperature. C.O.C.

Effect of Thickening Agents in Padding with Ultrasperse Vat Dyes

R. Kern

Amer. Dyestuff Rep., 48 (12) (15 June 1959) 57-61
Work done on use of thickening agents in the padding liquor as a means of checking migration during the intermediate drying after padding in the continuous dyeing of cotton cloths. C.O.C.

Fibres containing Active Methylene Groups and a New Dyeing Process for them**I—Partial Acetoacetylation of Cotton with Diketene**

H. Iida, N. Kuwabara, and K. Konishi

Rept. Govt. Chem. Ind. Research Inst. Tokyo, 54 (June 1959) 182-188 (xix-xx)

Azo dyes bonded with the fibre are produced by the action of aromatic diazonium compounds on fibres containing an active methylene group. Acetoacetylation of cotton with diketene was studied as a method of preparing such fibres. It was found that—(1) Reactivity of diketene with cotton is weak in absence of a catalyst, but increases when a catalyst is present. (2) Sulphuric acid and sodium acetate are good catalysts for this reaction. (3) A mixture of hexane with a little benzene is a suitable solvent for diketene. (4) The partly acetoacetylated cottons, when the content of combined diketene is > 15% of the wt. of dry cotton, are colourless and suitable for this process. When there is > 15% of the combined diketene the fibre turns yellow, and with > 40% the fibre becomes brittle.

II—Dyeing Partially Acetoacetylated Cotton by Means of Formation of Azo Dye Bonded with Fibre

H. Iida and K. Konishi

Ibid., 189-194 (xx)
Aromatic diazonium compounds readily react with partly acetoacetylated cotton to produce azo dyes bonded to the fibre. The partly acetoacetylated cottons used should contain 2-6% of their dry weight of diketene. At > 6% diketene content dyeing affinity decreases. Yellows to reds are obtained with azoic developers, and yellows to greens with acid dyes containing a diazotisable amino group. The light fastness of the dyed cloths varies

with the diazonium compounds used for development; fastness to light ranges from 1 to 5-6. Fastness to washing is usually 4-5, but in a few cases is only 2-3.

III—Dyeing Partly Acetoacetylated Cotton by Formation of Formazane Bonded with the Fibre

H. Iida *Ibid.*, 195-198 (xxi)
Partly acetoacetylated cotton containing about 2-6% diketene was developed with diazotized anthranilic acid, 1-amino-2-hydroxy-5-benzenesulphonic acid and 1-amino-2-naphthol-4-sulphonic acid in ammoniacal solution. The dyed cloths were converted to metal complexes by treatment with aqueous solutions of Cu, Ni, and Co salts. The resulting coloured cloths were very fast to light and washing. They were mostly brownish, but that containing the nickel complex of formazane developed with anthranilic acid was a brilliant yellowish green. C.O.C.

Dyeing Glove Curl Cloth

Anon. *Dyer*, 122 (20 Nov 1959) 657-8
Describes the actual details of works practice in dyeing these knitted tubular fabrics having a cotton foundation and a worsted or worsted-mohair pile. C.O.C.

Dyeing Cotton Yarns

B. S. Higham

Dyeing and Finishing Symposium, Melbourne, 1959, pp. 77-97
Deals with preparation of the yarn, dyeing machinery, and the various types of dye now available to the dyer. C.O.C.

Production of Yarns for the Knitwear Industry

A. Croasdale

Dyeing and Finishing Symposium, Melbourne, 1959, pp. 1-20
An account of Australian practice in the bleaching, chlorinating and dyeing of slubbing and yarns of wool and man-made fibres. C.O.C.

Dyeing and Finishing of Knitted Fabrics

A. Datyner *Dyeing and Finishing Symposium, Melbourne*, 1959, pp. 37-53
A general survey of the dyeing and finishing of knit goods made from wool and/or man-made fibres. C.O.C.

Developments in the New Solvent Dyeing Process for Wool**I—Summary of Early Investigation and Use in Screen Printing**

F. G. Lennox and B. S. Harrap

Dyeing and Finishing Symposium, Melbourne, 1959, pp. 21-4

Acid dyes can be applied to wool from solution in cold formic acid. Dyeing is very rapid and there is no damage to the fibre. Considerable saving in steam is secured. Used in screen printing no preliminary chlorination is necessary nor steaming to fix the dye in the fibre and the method can be used on raised wool fabrics.

II—Continuous Dyeing on a Laboratory Scale

B. Milligan

Ibid., 25-9
The process is applied to the continuous pad dyeing of slubbing and fabric in pale to medium depths using 70-75% formic acid as the solvent. C.O.C.

Recovery of Formic Acid in a New Solvent Dyeing Process for Wool

B. W. Wilson

Dyeing and Finishing Symposium, Melbourne, 1959, pp. 31-6
Consideration of methods now available for recovery and reuse of formic acid as the solvent in wool dyeing. C.O.C.

Formation of Dyes on Wool

A. I. Levchenko

Tekhnol. tekstil. prom., No. 4 (11) (1959) 121-126
Two methods of forming dyes *in situ* on wool are described—(a) oxidation of simple intermediates, e.g. 3-amino-carbazole, by H_2O_2 or $\text{Na}_2\text{Cr}_2\text{O}_7$; (b) azoic coupling, using initially an ammoniacal naphthol solution. Recipes and fastness data are given. G.J.K.

Dyeing Silk with Afterchrome Dyes

Sh. Kh. Averbukh and M. K. Lepetkova

Tekhnol. tekstil. prom., No. 3 (10) (1959) 126-134
The mordant is first absorbed by the fibre as HCrO_4^- ions. This is then reduced to its trivalent form and

combines with the dye to form a lake. Optimum pH for absorption is 2.6-2.7 obtained with 2-3% formic acid. Temperature control is of less importance as absorption of mordant by silk occurs at any temperature between 20-100°C. Lake formation occurs only above 60°C. and is most efficient at 80-100°C. Increase of mordant in the bath increases the amount of chrome absorbed by the fibre and improves the fastness to washing. L.S.L.

Dyeing of Rayon with Particular Reference to Triacetate Fabrics

J. Rennie *Dyeing and Finishing Symposium, Melbourne, 1959*, pp. 55-66

A review of modern processing with emphasis laid on the precautions necessary to avoid faulty fabrics being produced. C.O.C.

The Dyeing of Difficultly-dyeing Fibres (Vinyon)

K. Yamada and C. Shihnomiya

J. Soc. Textile Cellulose Ind. Japan,

15 (Nov 1959) 917-922

VI—Condensation—Combination Dyes (1)

The formation of pigments on the fibre by combination of compounds of low molecular weight is attempted in order to obtain high fastness and deep dyeings. Vinyon was thus dyed with several components comprising *p*-benzoquinone (Q_1), *p*-nitrosodimethylaniline (N_1), 4,4'-bisdimethylbenzhydrol (H_1) plus 8 aromatic amines or 5 phenols. A brown is obtained with 2-2% resorcinol and 2-2% Q_1 in water (liquor ratio 20:1) at 90°C. Further treatment for 40 min. in 2-7% H_1 dissolved in CH_3COOH gives a navy-blue. If H_1 is replaced by N_1 , a blue-black is obtained.

VII—The Condensation—Combination Dyes (2)

Ibid., 922-925

The pigment formed by condensation and combination does not dye the fibre, but when produced *in situ* the fibre can be dyed deeply and quickly. Q_1 and N_1 are oxidising and condensing agents, the final colour depending upon the active group in the first component— Q_1 brown, H_1 and N_1 blue. These three active compounds readily react together on the fibre but have low light fastness.

VIII—Condensation Dyeings with Active Halogen Compounds

K. Yamada, C. Shinomiya, and M. Takase

Ibid., 926-930

A study of 14 halogen compounds and 15 amino compounds. It is found that condensation dyeings differ only slightly in hue. Strongly basic amines having a conjugated system are most effective. Halogen derivatives containing solubilising groups give good results on nylon, wool, and vinyon, but cotton is the most difficult fibre to dye. Of halogeno compounds, the hydrolytic constant and reactivity with benzidine in water are in the order—2-chloro-5-nitrobenzene sulphonic acid > picryl chloride > 2-chloro-3,5-di-nitrobenzoic acid > 2,4-dinitrochlorobenzene > 2-chloro-4-nitrobenzene sulphonic acid > 1-chloro-2-nitrobenzene-4-sulphonamide. L.P.

Continuous High Temperature Dyeing of Capron Fabrics

E. I. Martsinkonene and A. I. Vaidakavichyus

Tekstil. prom., 19 (Sept 1959) 46-48

Pale and medium dyeings on Capron fabrics were obtained by padding with acid, disperse, and direct dyes, drying and heat-setting at 195-200°C. by infrared radiation. With acid and disperse dyes the fastness to wet processing was 5 and with direct dyes 4. G.J.K.

Textile Chemical Investigation. II—Mechanism of Dyeing Polyamide Fibres with Acid Dyes

G. Baek and H. Zollinger

Chimia (Switz.), 13 (1959) 100-1

Chem. Abs., 53 (10 Nov 1959) 20810

Experimental dyeings have confirmed that in aqueous medium at 100°C. nylon 66 exists as an amphoteric ion. C.O.C.

Use of Carriers in Dyeing Polyester Fibres with Disperse Dyes

E. Frierer

Reyon, Zellwolle u. Chemiefasern, 9 (1959) 378-383

Chem. Abs., 53 (10 Nov 1959) 20810

The three steps occurring in the process which are dependent on concentration are—(1) establishment of equilibrium between the surface layer of the fibre and the

carrier, water, and dye; (2) diffusion of carrier into the fibre with consequent loosening of the bonds between the polyester chains; and (3) diffusion of dye into the fibre. The action of the carrier is to transfer the dye from the bath into the hydrophobic fibre; this results from the swelling action of the carrier and its affinity for both dye and fibre; predominance of one or other effect depends on the structure of the dye and the fibre. The carrier introduces dye molecules on to the fibre surface where they deposit as a monomolecular layer and the simultaneous lowering of surface tension permits them to diffuse into the fibre micelles. The structure of the carrier is not so important as the number of carrier molecules dissolved in the fibre. Carrier properties of importance are affinity, cost, non-toxicity, high m.p., good emulsifiability, non-volatility, and ease of removal after dyeing. A list is given of all known carriers, with formulae, physical properties, trade names, amount used, advantages, and disadvantages. C.O.C.

Applying Acid and Copper-complex Dyes to Acrylic Fibres by a Cuprous Ion Process

J. Kachoyon and J. P. Niederhauser

Reyon, Zellwolle u. Chemiefasern, 9 (1959) 372-8

Chem. Abs., 53 (10 Nov 1959) 20810

The fibre is dyed in a bath, liquor ratio 1:10-20, containing a copper salt and 1-10% hydroxylamine sulphate on the weight of the fibre, for 30-60 min. at 120-130°C., rinsed, soaped at 60°C., rinsed and dried. The following dyes are applicable by this process—metallised (1:1) acid dyes, direct dyes with a Cu complex base, Cu phthalocyanines, and acid dyes. Dyeings on Orlon 42 by all these types of dyes have excellent fastness to washing at 60°C. and to sublimation. Fastness to light varies according to the dye. Use of high temperatures and hydroxylamine sulphate as the reducing agent increases the colour value of many dyes. Self dyeings lack liveliness and mixtures have to be used, levelling is satisfactory and shading is possible. The process can be used with blends of acrylic fibres with cotton but not with wool. In addition to good colour value there is uniform penetration and a certain antistatic effect. Loss in strength of Orlon 42 dyed in this way is comparable with that occurring when applying acid or basic dyes at 115°C. Acrylic fibres treated with hydroxylamine have some of their nitrile groups having acid or negative properties changed into groups having basic or positive properties; this explains the affinity for anionic dyes and the decrease in the hydrophobic character and static charge. C.O.C.

Dyeing of Vinyon with Direct Dyes. I—The Relation between Salt-Dye Ratio p and Substantivity Ratio q

A. Katayama, N. Kuroki, and K. Konishi

J. Soc. Textile Cellulose Ind. Japan,

15 (Dec 1959) 1007-1011

The salt-dye ratio $p = [Cl]/[D]_s$, and the substantivity ratio $q = [D]_f/[D]_s$ have been found for equilibrium absorptions of C.I. Direct Yellow 12, C.I. Direct Red 1, and C.I. Direct Red 2, for various salt concentrations at 90°C. A linear relationship was found between $\log p$ and $\log q$ at all observed salt concentrations. These results agreed with the theoretical deduction that the relation between p and q is independent of composition of the equilibrium solution. For C.I. Direct Yellow 12 this relationship, although linear, was salt concentration dependent. Discrepancy was attributed to increased chemical potential of dye in solution caused by suppression of hydration in presence of salt, and decreased potential dye in fibre.

II—Dyeing in the Absence of Salt

Ibid., 1011-1014

Absorption isotherms of C.I. Direct Red 1 and C.I. Direct Red 2 on Vinyon were obtained at 90°C. in absence of salt. The results were not in agreement with direct dyeing theory, the expression for amount of dye absorbed at equilibrium approximating to

$$[D]_F = \frac{K[S][D]_S}{1 + K[D]_S} + K'[D]_S$$

The heat of dyeing of C.I. Direct Red 1 was found to be dependent upon concentration of dye absorbed. It was suggested from these results that Vinyon contains a small number of active sites and a larger number of weaker sites of absorption. The affinity corresponding to the less active sites was considerably smaller than that obtained in presence of salt, this being explained by the assumption

that addition of salt raised the affinity of the dye on Vinyon as shown in Paper I above. F.J.

History of the Development of Bonded Fibre Fabrics at Minnesota Mining & Mfg. Co. and their Dyeing

B. E. Frank

Amer. Dyestuff Rep., 48 (14) (13 July 1959) 51-2

A brief account of the development of bonded fibre ribbons including their dyeing. C.O.C.

Blends of "Polyfibers" with Cotton. Advantages—Dyeing and Finishing Techniques

M. Santymire

Amer. Dyestuff Rep., 48 (12) (15 June 1959) 45-50

An account of the practice advocated by du Pont's Technical Service Section. C.O.C.

Knit Goods of Orlon Acrylic Fibre—Processing and Dyeing

G. R. Turner

Amer. Dyestuff Rep., 48 (14) (13 July 1959) 48-50, 52

An account of recommended U.S. practice including lists of suitable dyes. C.O.C.

Diazotisation and Coupling of Copolymers based on Acrylonitrile and *p*-Aminostyrene

G. I. Kubryetsov, E. A. Vasilyeva-Sokolova, and M. A. Zharkova

Zhur. priklad. khim., 32 (Nov. 1959) 2594-2597

Purified acrylonitrile was polymerised with *p*-aminostyrene in aq. emulsion at 60°C. for 3 hr. in presence of azo-isobutyric dinitrile (0.3%) as initiator and lauryl mercaptan (0.2%) as mol.wt. regulator. Monomer to water ratio was 1:5 and of acrylonitrile to *p*-aminostyrene 98:2 and 70:30 respectively. White or cream powders soluble in 50% H_2SO_4 were obtained. Polymer diazotisation was carried out with $NaNO_2$ at 0°C. using H_2SO_4 . Adding the diazotised polymer to 2 naphthol-3,6-disulphonic acid, β -naphthol, phenol, and acetyl-H-acid soln. resulted in the polymer being coloured fast to hot acids, alkali, organic solvents, and dry heat. T.Z.W.

Why Does the Fluorescence of Fluorescent Brightening Agents on Cloth Reach a Limit?

E. Allen

Amer. Dyestuff Rep., 48 (14) (13 July 1959) 27-9

Fluorescence reaches a limit at high concentrations of the agent on the fibre because almost all the available ultraviolet radiation used for exciting the fluorescence is absorbed at high concentrations and additional fluorescent brightening agent cannot absorb any more. The shape of the fluorescence v. concentration curve on cotton cloth can be fairly well predicted on the basis of the Kubelka-Munk reflectance law. C.O.C.

Practical Experience with the Pad-Roll Dyeing Machine

F. J. Percarpio, R. M. Lesh, and J. S. Thackrah

Amer. Dyestuff Rep., 48 (15) (27 July 1959) 41-3

An account of experiences with this machine in two U.S. dyeworks. C.O.C.

Spectrophotometric Colour Matching

M. V. Parjaneva

Tekstil. prom., 19 (Sept 1959) 44-46

Dyeing recipes for wool using 3 acid dyes (blue, yellow, red) have been derived using the dye absorption coefficients of the sample to be matched. The relationship between concn. and coefficient of the primary colours is expressed mathematically and graphically. Examples of matched dyeings are given, the single operation of matching requiring only 5-10 min. G.J.K.

Dyeing Cloth Continuously in Rope Form

E. Stanway

BP 818,332

The cloth is fed into the machine in continuous rope form along a trough through which liquor is circulated, to fold the cloth into a perforated compartment at one side of the machine, the trough being given an arcuate movement longitudinally of the machine. C.O.C.

Colouring Cellulosic Textiles with Azo Dyes containing a Sulphonfluoride Group

ICI

BP 819,320

An azo dye containing at least one ionic solubilising group and at least one sulphonfluoride group is applied from aqueous solution in presence of an acid binding agent. Thus cotton cloth was padded at 50°C. with an aqueous

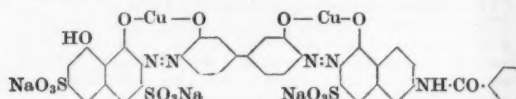
solution of the yellow dye 3-amino benzenesulphonfluoride \rightarrow 1-(4'-sulphophenyl)-3-carboxy-5-pyrazoline and 0.2% of a highly sulphonated oil. It is dried by continuous passage through a hot flue dryer at 110°C. The cloth is then padded at room temperature with an aqueous solution containing 1% NaOH and 30% NaCl, and washed successively in water, 2% aq. $NaHCO_3$, boiling 0.2% soap solution, rinsed and dried. This yields a bright yellow dyeing fast to light and mild washing. C.O.C.

Continuous Dyeing of Cellulosic Fabrics

Ciba

BP 817,864

The fabric is impregnated with a drop-forming liquid, neutral to alkaline, aqueous mixture containing a nickel or copper complex of an azo direct dye and an amine of formula $C_nH_{2n+1}(NH-CR^1R^2-CH_2OH)_2$ ($R = H$, Alk of < 4 C or oxymethyl; $R^1 = H$ or CH_3 ; $n = 1-4$) followed by fixation of the dye in a gaseous or a non-aqueous liquid medium. Thus cotton cloth is padded with an aqueous solution of the dye—



1,2-di(β -oxyethylamino)-ethane, monoethanolamine and tetrasodium pyrophosphate, at 80°C. After passing through the air for 30 sec., it is steamed for 2 min. at 105°C., rinsed, and dried. This yields a dark blue dyeing of the same depth as that obtained by using the same quantity of dye in a conventional direct dye bath. C.O.C.

Dyeing Keratinous Fibres

Société Monsaron l'Oreal

BP 819,814

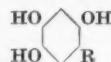
Nitro, azo, anthraquinone, disperse, basic, metal-complex, nigrosine or indoline dyes are used at low temperatures, e.g. for a woman's hair, by applying them in an aqueous solution or dispersion containing 5-20% on the weight of the solution of an organic solvent of formula $R(O-CH_2-CH_2)_nOH$ ($R =$ monovalent aliphatic or araliphatic hydrocarbon of < 9 C; $n = 1-4$), e.g. Butylcellosolve or Carbitol. C.O.C.

Trihydroxyphenols as Oxidation Bases in Hair Dyeing

Monsaron l'Oreal

BP 827,439

The hair is treated simultaneously with a compound of formula—



($R = H$, Hal, Alk, alkoxy or hydroxyalkyl) and an alkali metal or ammonium iodate, periodate or persulphate in aqueous medium at $> pH 7$. Thus 1,2,4-trihydroxybenzene (3 g.), acetic acid (2 g.) is dissolved in water (100 c.c.). Immediately before use sodium iodate (1.5 g.) is added to the solution. The solution has pH 4. White hair treated with this solution for 15 min., rinsed, washed, rinsed, and dried is dyed light chestnut having a golden tinge. C.O.C.

Recent Advances in Dye Technology (IV p. 245)

Yellow to Orange Disperse Dyes (IV p. 247)

Fluorescent Brightening Agents for Polyester Fibres (IV p. 247)

The Medieval Cloth Trade at Rouen (VI p. 249)

The "Rouennerie" Trade and its Entrepreneurs (VI p. 249)

John Holker, a Promoter of the French Textile Industry (VI p. 249)

Relation between Dye Absorption and Cotton Fibre Properties at Equilibrium (VI p. 250)

Decorative Fabrics from Fibrous Glass—Coronizing Process and Coro-Dyed Yarns (X p. 257)

Symposium on Non-woven Fabrics (X p. 257)

IX—PRINTING

The Normandy Textile Printing Industry of the Eighteenth and Nineteenth Centuries

H. Wescher

Ciba Review, 12 (135) (Dec 1959) 27-33

An account, illustrated in black and white and in colour, of the textile printing industry in Rouen from its first mention in 1688-9 to the end of the nineteenth century. C.O.C.

Properties of Printing Pastes

F. I. Sadov and E. O. Vil'dt

Tekhnol. tekstil. prom., No. 3 (10) (1959) 121-125

The important properties of printing pastes are briefly discussed. An oil-in-water emulsion type paste was prepared by emulsifying paraffin in ammoniacal casein. This has been evaluated and compared with pastes prepared from (a) maize starch, (b) sodium alginate, (c) cellulose ether (Preparation KTCM), (d) chitosan. Viscosity, degree of orientation, stability, and penetration of paste into fabric were examined. A 2.5% oil-in-water emulsion paste was stable and had viscosity similar to that of a 12% solution of Preparation KTCM. Penetration was less than that with other pastes under test. L.S.L.

Properties of Thickening Agents and Printing Colours

F. I. Sadov and Sin Men Khen

Tekhnol. tekstil. prom., No. 5 (12) (1959) 111-116

The adhesive properties (AP) of thickening agents and printing colours are investigated by means of a briefly described apparatus measuring the force (g./sq.cm.) required to separate (to 0.1 mm.) a film of thickening agent. With tragacanth and starch the AP conen. curves show a max. at 6% and 8% respectively, whilst with dextrin a continuous rise of AP with conen. occurs. An analogous finding applies also to printing colours. Mixtures of starch and dextrin show decrease in AP compared with that of each component. G.J.K.

Technology of Colour EmbossingP. I. Kon'kov *Tekstil. prom.*, 19 (12) (Dec 1959) 51-53

A detailed account of plant and practice in colour embossing cotton fabrics. Fabric was impregnated with a thermosetting resin (carbamide type), dried at 60-70°C., embossed and printed on a calendar equipped with a colour tray and three rollers for uniform transfer of printing paste on to the embossing roller, infrared dried (5-7 sec.), baked at 140°C. for 3 min. and washed off at 50-60°C. in alkaline soap solution (3 g./litre). The calendar pressures used were 20-180 kg./cm. and the speed 10-12 m./min. A whole range of direct and vat dyes and pigments was successfully applied. At higher embossing temperatures glycerine was used instead of water in the printing pastes. Lustre, colour, and embossed effects were obtained simultaneously by a slightly modified technique, i.e. embossed and printed with a mixture of dye and resin, dried, baked, and treated relaxed with 29% solution of caustic soda at 10-15°C. on a three bowl calendar (20 m./min.), washed off on a continuous washing machine (adding 5 g./l. acetic acid to the last bowl) and dried. Mercerising and washing off without tension caused considerable shrinkage of the unprinted part of the fabric. L.S.L.

PATENTS**Borohydrides as Reducing Agents for Vat Dyes in Textile Printing**

F.B.Y. BP 818,790

Alkali metal and alkaline earth metal borohydrides are very useful reducing agents when printing with vat dyes. Thus cotton cloth is printed with a paste made up of K_2CO_3 , NaOH, KBH_4 , thickener and C.I. Vat Yellow 1, dried, steamed at 102°C. for 5-10 min. in a rapid ager, rinsed, treated for 2-3 min. at 50°C. with dil. aq. hydrogen peroxide and acetic acid, and rinsed. C.O.C.

Textile Printing Emulsion

United Merchants and Manufacturers USP 2,894,801

Incorporation of 0.5-15.0% of a water-soluble casein compound into an aqueous solution containing a water-soluble formaldehyde sulfoxylate reducing agent followed by emulsifying the solution in a hydrocarbon oil to produce an oil-in-water emulsion, yields an emulsion which is stable even when large amounts of electrolytes are in solution in the aqueous phase. The casein compound minimises oxidation of the reducing agent, and does not form water-insoluble resins with the reducing agent. Such emulsions are good vehicles for vat dyes to be padded or printed on textiles. C.O.C.

Oil-in-water Emulsions for Printing Textiles

Gy BP 824,277

Use of a resinous binder comprising a thermosetting organic solvent-soluble amino-aldehyde resin (18-35% of the wt. of the binder), a fatty acid ester resin and an

elastomer, yields prints of improved resistance to wet and dry abrasion. There is also the advantage that the binder cures at a low temperature. C.O.C.

Screen Printing Plywood Wall Panelling

Pacific Wood Products Co. USP 2,897,040

Wood panels are screen printed with alcohol-soluble azo dyes, the alcohol solution being thickened with resin which preferably contains cellulose groups. A suitable vehicle is ethyl cellulose (1 part by wt.), ethylene glycol monoethyl ether (20), isopropyl alcohol (5), diethylene glycol monoethyl ether (5), and plasticiser (0-25). The printing pastes are made up of this vehicle (1590) and dye (22). C.O.C.

Photocopying Material

Ozalid Co. BP 826,005

A support sheet, e.g. cloth, paper or plastic film, is coated with a finely divided mineral, e.g. silica or alumina, and then with a photographic emulsion. Prints made from the resulting material have a much smoother background as application of the mineral has increased the mattness of the support surface. C.O.C.

Diazotype Materials containing Water-insoluble Synthetic Resins having Cation Exchange Properties

Ozalid Co. BP 818,911-2

Semi-wet Developing Process and Apparatus for Diazotype Reproductions

Charles Bruning Co. BP 818,017

Multi-layer Colour Photographic Material

VEB Filmfabrik Agfa Wolfen BP 818,233

Pressure-sensitive Record Material

National Cash Register Co. BP 825,354

A base material is coated with a solid, particulate, colour-reactant acid clay mineral and numerous oil-containing microscopic capsules formed by coacervation of an emulsion of oil and a hydrophilic colloid. Each capsule contains a colour reactant substance dissolved in the oil and each capsule breaks under normal writing pressure. Between the capsules and the clay mineral there is a material which is inert to pressure at normal temperatures but which is responsive on being warmed, e.g. a polyvinylmethylether. The resultant record material is uninfluenced by writing or typing at normal temperature but begins to mark when written or typed on when warm, e.g. when used on a heated backing plate or on application of a heated style or type. C.O.C.

Dry-release Transfer

Associated Trapinex BP 827,313

The transfer material is applied to a paper backing impregnated, or coated at least on the surface to which the transfer material is applied, with a polymerised silicone. This yields a transfer capable of dry release even at high speeds and under application of low pressure. C.O.C.

Surface Treatment of Organic Thermoplastic Films to

Render them Receptive to Printing Ink (I p. 243)

Printing or Decorating Ceramics, Glass, Plastics, etc. (I p. 243)

Acid Salts of Triarylmethane Basic Dyes for use in Spirit

Reproducing Transfer Materials (IV p. 247)

Photosensitive System consisting of a Heteropolytungstic

Acid and an Oxidisable Organic Substance (IV p. 248)

Developments in the New Solvent Dyeing Process for

Wool (VIII p. 252)

Colouring Cellulosic Textiles with Azo Dyes containing a

Sulphonfluoride Group (VIII p. 254)

Decorative Fabrics from Fibrous Glass—Coronizing

Process and Coro-Dyed Yarns (X p. 257)

Symposium on Non-woven Fabrics (X p. 257)

X—SIZING AND FINISHING**Cross-linking Cotton Fabrics with Aqueous Formaldehyde to Impart Wet Crease Recovery**J. D. Guthrie *Text. Research J.*, 29 (Oct 1959) 834-836

Laboratory and semi-bulk experiments are described and discussed. S.B.D.

Reaction of Formaldehyde with Cellulose

K. V. Datye and G. M. Nabar

Text. Research J., 30 (Jan 1960) 72-73

A brief outline of the study of the kinetics of the reaction in an idealised system. S.B.D.

Dimensional Stabilisation of Knitted Cottons

B. J. Roberts

Dyeing and Finishing Symposium, Melbourne,

1959, pp. 99-109

A brief account of resin finishing and the control tests necessary. C.O.C.

Dimensional Stabilisation of Spun Rayon Fabrics

P. J. Ambry

Dyeing and Finishing Symposium, Melbourne,

1959, pp. 67-75

Residual shrinkages of < 2% are obtained with a variation between batches rarely > 2% if care is taken to process the cloth at its fully relaxed width, fully relax warpwise before curing, make sure that the cloth is at or just below pH 7 before impregnating with the resin, and that curing is complete. C.O.C.

Tetrahydropyrimidinone Derivatives for Non-chlorine Retentive, Crease-shedding Cotton Fabrics

J. G. Frick, B. A. Kottes and J. D. Reid

Amer. Dyestuff Rep., 48 (13) (29 June 1959) 23-5

Use of the dimethylol derivative of tetrahydro-5-hydroxy-2(1H)-pyrimidinone yields a crease-shedding, wash-and-wear finish which does not retain chlorine even after repeated hot, alkaline launderings. In addition it does not yellow on heating and there is no residual odour. It is, however, susceptible to hydrolytic removal at < pH 4. C.O.C.

Mechanisms Influencing the Wash-and-wear Characteristics of Cellulosic Fabrics

C. R. Williams

Amer. Dyestuff Rep., 48 (12) (29 June 1959) 27-30, 39

There are two different mechanisms of fabric distortion: (1) internal to the fabric and (2) external to the fabric. Rendering the fabric dimensionally stable prevents development of internal forces and high crease-recovery minimises external distortions. Good wash-and-wear appearance after laundering demands both dimensional stability and high wet crease recovery but is probably not dependent on high dry crease recovery. All three physical properties are necessary for good wash and wear performance. C.O.C.

Synthetic Resins for Chlorine-fast "Wash-and-Wear" Finishes

H. Enders and G. Pusch. Translated by E. A. Parolla and C. Z. Draves

Amer. Dyestuff Rep., 49 (1) (11 Jan 1960) 25-38 (1-14)

Translation of article previously abstracted, see J.S.D.C., 75 (1959). C.O.C.

Relation of Wet and Dry Crease Recovery to Wash-and-wear Behaviour

R. Steele

Text. Research J., 30 (Jan 1960) 37-46

The chemical changes in cellulose fibre which lead to various wet to dry crease recovery ratios are reviewed. Covalent cross-linking of a dry fibre increases both wet and dry recovery, and the ratio of the two values is believed to depend on the relative accessibilities of the fibre to water and to the cross-linking agent. Water-sensitive links between cellulose chains give a low value to the wet-dry crease recovery ratio, whilst cross-linking reactions carried out when the fibre is wet give a high value. To achieve good wash-wear behaviour both wet and dry crease recovery must be increased and for tumble-dry methods their ratio should be around unity. For drip-dry methods the wet crease recovery is of more significance than the dry. S.B.D.

Chlorine-resistant Blends of Triazone and Urea Derivatives for Crease-shedding Cotton Fabrics

J. G. Frick, R. L. Arceneaux, R. M. Reinhardt, and J. D. Reid

Amer. Dyestuff Rep., 48 (15) (27 July 1959) 29-31, 36

Mixtures of the methylol derivatives of purified ethyl-triazone and urea can contain up to 50% of the urea-formaldehyde component without the finish being very chlorine retentive. Their use necessitates greater care in selection of catalyst and in processing. Blends of methylol derivatives of ethyl triazone and ethyleneurea are more resistant to hydrolysis than a straight ethyleneurea finish but have no advantage over the straight triazone finish. C.O.C.

Soil-resistance of Resin-finished Fabrics. II—Combined Effects of High Polymer Electrolytes with Dimethylol-ethylene-urea

T. Matsukawa

J. Soc. Textile Cellulose Ind. Japan,

15 (Dec 1959) 1001-1006

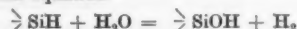
Resin-finished cotton fabrics treated with high polymer electrolytes, Na-CMC (I) Na-alginate (II) copolymer of vinyl-methylether and maleic anhydride (III) or copolymer of vinyl acetate and Na-maleate (IV) showed improved soil-resistance measured by reflectance differences. When these electrolytes were added to dimethylol-ethylene-urea (V) in the treatment of fabrics there was a loss in crease-resistance compared with treatment using (V) and ordinary acrylic polymers. From conductometric measurements it was considered that (V) reacted especially with (II) and (III) to reduce the amount of (V) which would normally be available for cross-linking. F.J.

Water-repellent Treatment of Textiles with Silicones—Mechanism of Gelling-type Processes

J. A. C. Watt

J. Textile Inst., 52 (Jan 1960) T 1-T 16

Gelling of polymethylsiloxane fluids with stannous, zinc or lead salts of organic acids, occurring during water-repellent finishing, proceeds by means of base-catalysed hydrolysis in which the partly hydrolysed metal salt acts as base. With zinc and lead salts evolution of gas proceeds fairly smoothly and gelation occurs after liberation of sufficient hydrogen to account for at least one cross-link per molecule. With stannous salts gelation is quicker and occurs before sufficient hydrogen has been liberated to account for one cross-link per molecule, after which the volume of gas liberated quickly reaches a value corresponding to the equation—



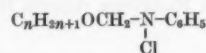
Further slow liberation of gas is attributed to the same reaction occurring between the Si-H bond and water liberated by condensation of silanol groups or to direction combination of silanol with the Si-H bond. This agrees with the behaviour of polymethylsiloxane + catalyst on cloth when a large proportion of the active hydrogen is liberated early on in processing but water-repellency is not developed until baking or ageing is completed. Hence requirements of a catalyst for polymethylsiloxanes are solubility in the siloxane system and basicity, to bring about conversion of $\geq \text{SiH}$ group to silanols and also to condense the silanols to siloxanes. Stannous salts seem also to cause abnormally rapid solidification of polymethylsiloxane fluids even under anhydrous conditions, but the mechanism of this reaction has not yet been discovered. C.O.C.

Combined Water- and Rot-proof Finish for Canvas

N. V. Kalugin

Tekstil. prom., 19 (Aug 1959) 40-41

Grey, scoured and mercerised canvas fabrics impregnated with a 3% solution of preparation 246, viz.—



($n = 12-18$), are rendered water-proof after heating at 110-115°C. Size and impurities interfere with the durability of the finish. The resistance to water and rotting is noticeably improved by using a combined impregnation with preparation 246 and Latex SVKh. G.J.K.

Rot-resistant Finishes for Cotton

A. Ruperti

Text. Research J., 30 (Jan 1960) 68-69

W. N. Berard, G. A. Gautreaux, and W. A. Reeves
Ibid., 70-71

The advantages and disadvantages of a formic acid-methylolmelamine acid colloid finish are discussed. S.B.D.

Continuous Carbamoylmethylation of Cotton Fabric—Preliminary Cost Study

K. M. Decossas, O. J. McMillan, W. A. Reeves, J. D. Guthrie, and E. F. Pollard

Amer. Dyestuff Rep., 48 (14) (13 July 1959) 30-1**Finishing Woollen and Blended Fabrics**

C. S. Whewell

Canadian Textile J., 75 (26 Dec 1958) 37-45

A review (15 references) of the finishing of woollen and blended fabrics. Crabbing, wet or dry blowing or pressure steaming are all employed in the setting of woollens. In

wet processes pH 8-4 is optimum. In Europe, Terylene-wool blends are commonly stenter-set at 220°C. since low pressure steaming is inadequate and high pressure steaming causes degradation and nylon-wool blends are also dry-set at 170°C. for 3 min. up to 230°C. for 10 sec. Steam-setting at 30 p.s.i. can, however, be successfully applied to the latter. British practice, however, is to set by dry blowing. Blends of wool with acrylic or cellulose triacetate fibres require minimal treatment to avoid difficulties in subsequent permanent pleating. Wool blends are more difficult to scour than pure wool and generally show similar or less shrinkage. Soap and cationic detergents are valuable assistants in milling and felting in contrast to synthetic anionic detergents. Pilling is difficult to avoid entirely but is less with high twist yarns and tight weaves. Close-cutting and singeing assist by reducing loose surface fibres. Shrink-resistance can be achieved by melamine-formaldehyde resins or by methylolnylons. Polymerisation of monomers absorbed in wool fibres leads to increase in stiffness and in fibre diameter and to reduction in water absorption but has no effect on crease-resistance. In dyeing processes, use of syntans in the dyebath (Maifoss process) gives an uneven resist and with suitable dyes can produce Lovat effects. Resist effects on wool can also be obtained with bromoacetic acid or by treatment with conc. sulphuric acid followed by immediate neutralisation.

E.C.

Resin Coating and Resin Treatment of Textiles

G. W. Benkendorf

Textile J. of Australia, 34 (20 June 1959) 499-507
A review (24 references) of the structure of synthetic resins and the use of plasticisers with particular reference to the application of polyvinyl chloride dispersions in plasticisers (plastisols) and in volatile liquids (organosols) to fabrics by doctor knife coating, roller coating and impregnation and to the chemistry of urea, melamine, and cyclic ethyleneurea condensation with formaldehyde with a brief note on the value of these resins in textile treatment.

E.C.

Milling

R. Schmidt

Tint. Ind., 46 (Sept 1959) 455-472

A general description of the milling of cloth of different weights, of dyed material and of wool-viscose unions. One section is devoted to related machinery and a further section to the use of some proprietary brands of auxiliaries in milling under alkaline, neutral, and acid conditions.

F.J.

Development of Washable Non-iron Effects in Pure Wool Fabrics

A. J. Farnworth, M. Lipson, and J. R. McPhee

Text. Research J., 30 (Jan 1960) 11-22

Use of reducing agents for setting wool has been extended to give washable non-iron effects on pure wool fabrics. Initially this was accomplished by applying the Si-Ro-Set process to garments made from shrink-resisted wool. This led to flat setting in the mill by applying a dilute soln. of reducing agent to the fabric then immediately steaming. When preceded by shrink-resisting this method of setting gave excellent washable non-iron effects. Garments made from treated fabric showed satisfactory laundering and wearing performances in practical trials.

S.B.D.

New Approach to Fabric Pest Control

R. J. Pence

Soap Chem. Specialities, 35 (8) (1959) 65-8, 105-6*Chem. Abs.*, 53 (25 Oct 1959) 19284

The nutrient value of contamination as a source of food for fabric pests is divided into direct and indirect categories. The rôle of vitamin synthesis of micro-organisms is considered to be the source of indirect contamination. In both cases the yields of nicotinic and pantothenic acid are vital to fabric pest development. Antimetabolites when incorporated into a fibre diet caused feeding insects to die of starvation.

C.O.C.

Improving the Light Fastness of Nylon

T. Hashimoto

IV—Acetylation

J. Soc. Textile Cellulose Ind. Japan,

15 (Nov 1959) 897-902

Acetylation of nylon taffeta by acetic anhydride affects the amino end-groups but not the amide link. This can be deduced from the only slightly increased weight and

change in N-content. Acetylation affects the stress-strain curve and absorption of H^+ , H_2O and disperse dyes. The rate of acetylation is proportional to the concentration of unacetylated amino end-groups until this exceeds 50%.

V—Alkali Treatment

Ibid., 902-905

The light resistance of nylon taffeta is increased by treatment with aq. NaOH and temperature enhances this effect. LiOH and KOH behave similarly but Na_2CO_3 and $NaHCO_3$ are ineffective. Hydroxyl ions are absorbed by the fibre, and as the OH^- concentration and time of treatment increase, the alkali exhaustion approaches a saturation value approximately equal to the COOH content of nylon.

L.P.

Schreiner Finish on Nylon Tricot

D. Hardisty *B.N.S. Outlook*, 2 (Winter 1959/60) 29-35

The advantages of Schreiner calendaring on the properties of warp-knitted nylon fabrics, e.g. improved appearance, handle, and opacity, are discussed, and details of methods of fabric finishing are given.

W.G.C.

Mechanism of Tear in Industrial Coated Nylon Fabrics

V. K. Hewinson

B.N.S. Outlook, 2 (Winter 1959/60) 17-27

The factors affecting tear strength of industrial coated nylon fabrics are discussed—yarn properties, fabric structure, coating quality, location of coating, degree of penetration into fabric structure. The effect of outdoor exposure on the breaking load and tear strength of a number of coated nylon fabrics is tabulated.

W.G.C.

Ionic Deposition containing Carboxyl Groups. I—Coating Cloth with Rubber from Carboxylated Latex by Ionic Deposition

A. R. Kuznetsov, M. S. Monastyrskaya, and S. A. Pavlov

Kauchuk i Resina, 18 (1) (1959) 13-5*Chem. Abs.*, 53 (10 Nov 1959) 20873

Cloth can be coated with rubber by ionic deposition of carboxylated latex from stock SKS-5-30 with aq. $MgCl_2$ which acts both as coagulating and vulcanising agent. Adhesive strength between the rubber and cloth is greatly increased, from 400-1800 g./cm., by adding methacrylate or poly(methyl methacrylate) resin to the latex. It also increases as pH decreases. This method does not require the stabilising agents usually employed when vulcanising ingredients are added to latex.

C.O.C.

Decorative Fabrics from Fibrous Glass—Coronizing Process and Coro-Dyed Yarns

F. J. Lachut

Amer. Dyestuff Rep., 48 (12) (15 June 1959) 43-4, 50

A brief description of the manufacture of glass fibres and fabrics is followed by an account of the Coronizing process and production of Coro-Dyed yarns.

C.O.C.

Symposium on Non-woven Fabrics

I—Areas for Non-woven Fabric Advancement

P. A. Hornier

Amer. Dyestuff Rep., 49 (11 Jan 1960) 40-1 (16-17)

II—Properties of Acrilan Non-woven Fabrics as a Function of Fibre Length, Denier, and Binder Content

D. C. Nicely

Ibid., 41-3 (17-19)

III—Styling and Decorating Acetate Non-wovens

E. L. Clements, H. W. Coates, and C. E. Layman

Ibid., 44-6 (20-2)

Deals with solvent dyeing, screen and machine printing of acetate bonded fibre fabrics, plasticizer-dye-acetate rayon constructions and embossing.

C.O.C.

PATENTS

Water Repellent Finish

Calico Printers' Assocn.

BP 818,778

Cellulosic materials are treated with an alkylamine of $> 10^\circ C$ and a 1,3,5-triazine derivative having > 1 halogen substituent attached directly to the nucleus. They are then treated to cause the triazine derivative to condense with both the alkylamine and the cellulose. Thus cotton cloth was padded through 15% aq. Na_2CO_3 to 130% expression and dried. It was then padded to 108% expression with a solution made by dissolving cyanuric chloride (2 g.) in chloroform (100), cooling to 10-15°C. and then adding *n*-octadecylamine (3) in chloroform (100).

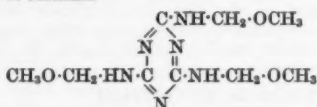
The cloth was then steamed for 30 min. and washed with hot water. It acquired an excellent water repellent finish which was improved by hot soaping and was not impaired by dry cleaning in trichloroethylene. C.O.C.

Water Repellent Cotton Textiles

General Electric Co.

BP 818,289

A water repellent finish resistant to repeated launderings is produced by impregnating a cotton textile with a compound of formula—



insolubilising this compound in the fibre, treating with an alkyl hydrogen polysiloxane containing by weight 0–200% of an alkyl polysiloxane free of Si-bonded hydrogen and finally baking at $> 100^\circ\text{C}$. C.O.C.

Bulking and Lofting Wool Textiles

U.S. Secretary of Agriculture

USP 2,895,286

Wool yarn is treated with a swelling agent, stretched and set while swollen, and finally relaxed in absence of tension. This yields a yarn of much greater bulk, softness, and elasticity compared with the untreated yarn. The yarn may be, e.g. knitted or woven before being relaxed, in which case products of greater bulk, softer handle, and greater elasticity are obtained. C.O.C.

Organo-silicon Compounds for Setting Hair

Société Monsanto l'Oreal

BP 827,419

Hair can be durably set without being softened if it is treated with trimethylsilyl monomercaptoacetate, dimethylsilyl dimercaptoacetate or monomethylsilyl trimercaptoacetate in aqueous alkaline solution and presence of a compound which prevents or retards precipitation of the polymerising organo-silicon product of hydrolysis, e.g. alcohol. C.O.C.

Increasing the Resistance to Pilling and the Density of Fabrics of Polyester Fibre-Cellulose Blends

DuP

USP 2,897,042

The fabric is treated with an aqueous solution of a phenol or phenol substituted in any position with hydrocarbon groups of 1–6 C, e.g. *m*-cresol and *o*-ethyl phenol, for < 2 min. at $< 160^\circ\text{F}$. in absence of tension and so that the polyester fibres shrink on average $< 18\%$ in length, i.e. the fabric must shrink $< 22\%$ warpwise and $< 15\%$ weftwise. C.O.C.

Antistatic Finish

BASF

BP 819,021

Treatment in separate baths of highly polymeric organic cation-active and highly polymeric organic anion-active compounds imparts an antistatic finish which is fast to washing. Thus Perlon is treated first with poly(*N*-vinylimidazole), quaternised with dimethyl sulphate and then with a styrene-maleic acid copolymer. C.O.C.

Coated Fabric

H. Boivin

BP 824,214

A mixture of a synthetic resin and 0.5–1.0% of a blowing agent is spread on a textile backing, preferably a knitted fabric, below the activation temperature of the blowing agent. A fine powder is then sprinkled on the coating and while the backing is supported the temperature is raised to activate the blowing agent and set the resin. Finally the powder is removed. The powder may e.g. be NaCl and be removed by water. This yields a coated fabric which is stretchable and flexible, has a dull surface, and is permeable to water vapour. C.O.C.

Coating Fibres with Modified Butyl Rubber

Eso Research & Engineering Co.

USP 2,895,850

A strong bond between Butyl rubber and fibres, including man-made fibres, is obtained if the fibres are first treated with an aqueous solution of a phenolic-aldehyde resin, e.g. resorcinol-formaldehyde resin, dried and then coated with a Butyl rubber previously treated with 0.1–5.0% of a nitrosodihydroxy aromatic compound, e.g. *p*-nitrosophenol. C.O.C.

Permeable, Vinyl Resin-coated Fabric

B. F. Goodrich Co.

USP 2,894,855

A fibrous sheet, e.g. cloth or bonded fibre fabric, is coated with a layer of a foamable resinous or rubbery

coating composition which is caused to blow while under mechanical restraint imposed by (1) a pervious restraining device, e.g. a wire grid, placed directly against the uncoated surface of the sheet, and (2) an impervious restraining device, e.g. metal sheet, placed directly against the coating layer. The evolved gas is thus forced to escape through the sheet and in so doing form a multitude of very fine channels which are virtually invisible by reflected light and which impart excellent permeability to the coated sheet. C.O.C.

Coated Fabric

DuP

BP 819,460

Coated fabric highly resistant to abrasion on one side and weather resistant on the other and so useful as tarpaulin is obtained by coating a base fabric, preferably nylon, on one side with a natural or synthetic rubber and on the other with chlorosulphonated polyethylene. C.O.C.

Flocked Fabric

Carl Freudenberg

BP 819,333

Fabric with a flock surface of any desired thickness is obtained by applying the flock in two or more layers. To anchor the flock to the base and the flock layers to each other the adhesive is applied as fine drops which form a dew-like coating on the respective underlayers. C.O.C.

Bonded Fibre Fabric

Chicopee Manufacturing Co

BP 818,943

A web of fibres is impregnated with (1) 5–40% of its dry weight of a thermosetting melamine-, urea-, phenol-, or dicyandiamide-formaldehyde crease-proofing resin, and (b) as binder, a polymer or copolymer of an alkyl acrylic ester (Alk of < 9 C), the combined weight of resin and binder being 25–75% of the weight of the fabric. This yields a resilient crease-resistant fabric suitable, e.g. as an interlining, interfacing or bouffant material for garments or as a filter cloth. C.O.C.

New Sizing and Scouring Auxiliaries (III p. 243)

A Mild-cure Catalyst (III p. 243)

Latices in the Textile Industry (III p. 243)

Photosensitive System consisting of a Heteropolytungstic

Acid and an Oxidisable Organic Substance (IV p. 248)

The Medieval Cloth Trade at Rouen (VI p. 249)

John Holker, a Promoter of the French Textile Industry (VI p. 249)

Partly Carboxymethylated Cotton as an Intermediate for

Further Chemical Modification (VI p. 250)

Trifluoroacetic Anhydride for Partial Acetylation of Cotton Cellulose (VI p. 250)

Production of Yarns for the Knitwear Industry (VIII p. 252)

Dyeing and Finishing of Knitted Fabrics (VIII p. 252)

History of the Development of Bonded Fibre Fabrics at Minnesota Mining & Mfg. Co. and their Dyeing (VIII p. 254)

Blends of "Polyfibers" with Cotton. Advantages—

Dyeing and Finishing Techniques (VIII p. 254)

Technology of Colour Embossing (IX p. 255)

Photocopying Material (IX p. 255)

Symposium on Non-woven Fabrics (X p. 257)

Cross-linking Cellulosic Materials by Irradiation (XI p. 259)

Surface Chemistry and Adhesion of Polymers (XIII p. 259)

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Flow Behaviour and State of Solution of Cellulose in the Alkaline Iron-Tartaric Acid Complex

K. Edelmann and E. Horn

Faserforsch. und Textiltech., 10 (Nov 1959) 531–535

From studies of flow properties of solutions of cellulose nitrate in butyl acetate, in which the nitrate is molecularly dispersed, and those of cellulose in an alkaline solution of the iron-tartaric acid complex it is concluded that, in the latter case, the cellulose is dispersed as micelles or aggregates. W.R.M.

Change of the Reactivity of Ground Cellulose

V. I. Shorkov, I. I. Korolkov, and E. N. Garmanova
Zhur. priklad. khim., 32 (Nov 1959) 2586–2588

Natural cellulose, subjected to dry grinding, changes under the influence of absorbed moisture, losing its

reactivity to ethanolysis. The decrease of reactivity is very small at < 14% moisture content. Increasing the moisture content to 20% sharply diminishes cellulose reactivity. Aq. alcohols decrease the reactivity directly proportional to their water content. Organic liquids with a high dielectric constant (glycol, glycerin, formamide) act on ground cellulose similarly to water.

T.Z.W.

Synthesis and Properties of Alkyl Carbonic Esters of Cellulose

Z. A. Rogovin and Yu. S. Kozlova

Zhur. obsch. khim., 29 (May 1959) 1667-1671

Synthesis of methyl-(I) and ethyl-(II) carbonic esters of cellulose from alkali cellulose and esters of chlorocarbonic acid is described. The stability of I and II to detergents and to heating (100°C.) in air is shown to depend on the acid radical (carbonic or thiocarbonic acid) and the alkyl group. γ of I is 36-87; γ of II is 50-68.

G.J.K.

PATENTS

Cross-linking Cellulosic Materials by Irradiation

General Electric Co.

USP 2,895,891

When cellulosic materials containing no salt groups are irradiated in presence of water they cross-link and do not suffer degradation. The irradiated products are insoluble in water even when the original material was water-soluble. This enables soluble cellulosic materials, e.g. methyl cellulose, to be extruded from solution into a radiation field, dried and rolled on to suitable reels.

C.O.C.

Brightening Paper by Incorporation of Silica and Silicate Pigments

FBy

BP 819,361

The silica or silicate pigments obtained by precipitation from aqueous alkali metal silicate and of average particle size 0.03-0.3 μ . have a better brightening effect than anatase when incorporated into paper.

C.O.C.

Acid Salts of Triarylmethane Basic Dyes for use in Spirit Reproducing Transfer Materials (IV p. 247)

The Effect of Ionising Radiations on Cellulose (VI p. 250)

Photocopying Material (IX p. 255)

Optical Classification of Unbleached Sulphite Pulp (XIV this page)

Determination of pH of Paper with Coloured Indicators (XIV p. 260)

Evaluation of the Handle of Paper (XIV p. 260)

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Mechanical Properties of Raw Collagen Fibres

F. R. Morgan and R. G. Mitton

J. Soc. Leather Trades Chem., 44 (Jan 1960) 2-23

A report of a systematic study of the mechanical properties of acetone-dehydrated raw collagen fibres teased from cow-hide. Alternating stress and relaxation (conditioning) does not affect the breaking strength or extensibility of the fibre unless the conditions approach those which cause rupture. Strength and breaking extension tend to decrease with increasing fibre length and, on the whole, fibres of thin cross-section are relatively stronger than thick ones. Max. strength and extensibility are obtained when the loading rate is ca. 12 g./min., at which rate the breaking load probably depends upon inter-fibrillar sliding; above and below this optimal rate there are probably two different mechanisms of fibre breakage. Max. strength is obtained within R.H. 40-70% (though the variation is not large) but extension at break increases with humidity to a max. at 30% R.H. The critical rate of loading (12 g./min.) obtains below ca. 70% R.H.

J.W.D.

Zirconium Tannage—Effect of Particle Size on the Penetration of Zirconium into Pelt

D. A. Williams-Wynn and R. L. Sykes

J. Soc. Leather Trades Chem., 44 (Jan 1960) 23-32

Particle size is a major factor in controlling the rate of penetration of Zr into hide. Addition of dry Zr tanning salt ensures that the soln. is fresh and that the particle size is small. Complete penetration cannot be obtained with dil. soln. since particle size increases rapidly with lower concn. Addition of acid both reduces the activity of the collagen and ensures a relatively small Zr particle size in

soln. Determination of the particle size of Zr in soln. is described and discussed. Experimental evidence is presented in support of the above theory.

J.W.D.

PATENTS

Chrome Tanning

FBy

BP 827,430

Very light-coloured leathers are obtained by treating with a mixture of a normal or basic trivalent Cr salt, e.g. potassium chromium sulphate and chromium sulphate hexahydrate, and a tanning agent produced from a methylol compound of a phenol or of a phenol-sulphite and/or bisulphite condensate and then completing tanning by use of a vegetable and/or synthetic tanning agent.

C.O.C.

Coated Leather

Rubber Improvement

BP 819,203

The leather is coated with a paste consisting of a vinyl polymer or copolymer, plasticiser, stabilisers, and pigment with or without solvent. The deposited film is then anchored to the leather by heat fusion under pressure applied between the leather and a plate or matrix by a resiliently compressible pressure member acting on the uncoated side of the leather. The finish may be varied from glossy to dull or embossed depending on the surface of the plate used.

C.O.C.

New Waterproofness Tester for Gloving Leathers (XIV p. 262)

XIII—RUBBER; RESINS; PLASTICS

Surface Chemistry and Adhesion of Polymers

W. C. Wake

Trans. I.R.I., 35 (Oct 1959) 145-165

The nature of the interface and the concept of surface free energy are outlined and surfaces of high and low energy are discussed. Physical adsorption is considered and speculation on the possible rôle of chemisorption in particular cases is commented upon. The adhesion of flexible polymers such as rubber and poly(vinyl chloride) to textiles is discussed and the influence of the form of the textile is considered; use of specific adhesives is recommended but, in their absence, the adhesion of such a polymer to a textile (A) is given by the expression—

$$A = x (\text{interfacial surface area}) + y (\text{number of projecting fibre ends or trapped filaments})$$

where x and y are constants characteristic of the particular polymer-textile combination. Four methods for measuring the surface area (available to form an interface) are described and discussed in an appendix.

J.W.D.

PATENTS

Difficultly Imflammable Styrene Polymers

BASF

BP 825,611

Addition of an ester of 2,3-dibromopropanol-1 to a styrene polymer renders the polymer flame-resistant without altering either its mol.wt. or softening range.

C.O.C.

Surface Treatment of Organic Thermoplastic Films to Render them Receptive to Printing Ink (I p. 243)

Titanium Dioxide (C.I. Pigment White 6) for Pigmenting Synthetic Polymer Films or Sheets (IV p. 248)

Diazotisation and Coupling of Copolymers based on Acrylonitrile and *p*-Aminostyrene (VIII p. 254)

Photocopying Material (IX p. 255)

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Stability to Laundering of Fabrics made from Cellulosic Fibres

G. V. Land and W. T. Waters

Text. Research J., 29 (Dec 1939) 950-960

Laundry shrinkage of cellulosic staple fibre fabrics can be broken down into three components: (1) Fibre relaxation caused by relaxation of strains imposed on the fibres during processing, (2) Fabric relaxation caused by fibre and yarn swelling which results in crimp adjustment and consequent shrinkage, and (3) "felting" or "progressive" shrinkage caused by fibre movement. The second component depends upon the degree of swelling in water while the third component depends upon the ease of stretch of the wet fibres. Fibres of tenacity at 5% extension of 0.6 g./den. make fabrics which do not suffer from "progressive" shrinkage. Yarn and fabric geometry also affect both 2 and 3. Yarn and fabric construction giving more bulk and less compactness have less relaxation shrinkage potential. Factors facilitating relative fibre movement under severe agitation in water cause greater "progressive" shrinkage. Loose fabric construction and weave, highly twisted yarns with warp and weft yarns having the same direction of twist, finer denier, and longer staple length all tend to increase the "progressive" shrinkage potential of cellulosic staple fabrics. C.O.C.

Determination of pH of Paper with Coloured Indicators

R. Müller and J. C. Ulrich

Textil-Rund., 14 (Dec 1959) 703-704

Inflowing stock has often not the same pH as the finished paper. Spot tests with special indicators and comparison with standard colour charts provide means for rapid determination of the pH of the finished sheets so that adjustments can be made on the machine immediately. Colour interference and ring formation is avoided by using 0.5 g. Bromocresol Green in 500 ml. 10% alcohol, 0.2 g. Methyl Red (C.I. Acid Red 2), in 500 ml. 50% alcohol or 0.1 g. Chlorophenol Red in 500 ml. 20% alcohol. The latter is only suitable for pH 5.3-5.5 when it changes sharply from yellow through grey to violet. Good agreement was obtained when checking the aqueous extracts against glass or antimony electrodes, after the extracts had been evaporated down to the same concentration as obtained in the indicator measurements. R.A.

Evaluation of the Handle of Paper

L. Frossard

Textil-Rund., 14 (Dec 1959) 699-703

The Thwing-Albert Handle-O-Meter, described and illustrated, has been developed to measure stiffness and surface friction simultaneously to give numerical evaluation of the subjective concept of handle. As measurements are influenced by a number of known factors acting in unknown relationships, it is impossible to say whether the differences recorded by the instrument actually correspond to the practical and observable differences in handle, especially as the latter is also influenced by other factors not recorded by the instrument. The differences recorded cannot be attributed to any one of the known variables, e.g. furnish, sheet formation, beating, and moisture content. It is, therefore, not possible to correlate them with operating conditions. The Handle-O-Meter, primarily designed for the textile industry, may find some use in paper mills specialising in one type of paper only. R.A.

Polarographic Analysis of Driers

H. P. Kaufmann and M. Bernard

Fette, Seifen, Anstrichmittel, 59 (1957) 843-5
Chem. Abs., 53 (25 Oct 1959) 19403

Discusses the polarographic analysis of Pb, Fe, Co, and Mn naphthenates, linoleates, and octoates. Details of procedure are given together with 11 graphs. Results obtained are compared with those obtained by gravimetric methods. C.O.C.

Determination of Zirconium in Zirconium Driers. Ethylenediaminetetraacetic Acid Titration in 1 to 4 Sulphuric Acid

C. F. Hirn and C. A. Lucchesi

Anal. Chem., 31 (1959) 1417-8
Chem. Abs., 53 (10 Nov 1959) 20832

The drier (0.3 g.) is dissolved in 1:4 H₂SO₄, heated for 5 min. below b.p., excess of standard di-Na(ethylenedinitrilo)tetraacetate solution is added, boiled 5 min. and the excess tetraacetate back-titrated at pH 2 with standard

Bi(NO₃)₃ soln. to the thiourea end-point (Flaschka *et al.*, *Chem. Abs.*, 52 (1958) 18092). C.O.C.

A Paper-chromatographic Method for the Identification of α - and β -Naphthol when Present Together

M. R. Verma, Ranji Dass, and P. K. Gupta

J. Chromatography, 3 (Feb 1960) 197-199

A spot of 0.1% alcoholic solution of a mixture of α - and β -naphthol was placed on chromatographic paper. After coupling *in situ* with a cold alkaline solution of diazotised amino-J Acid and drying the spot was eluted with iso-amyl alcohol-ethyl alcohol-ammonia (40:40:25). The two components were resolved into two spots, amino-J acid \rightarrow α -naphthol, red, and amino-J acid \rightarrow β -naphthol, reddish orange. F.J.

Chromatography of Polycyclic Aromatic Hydrocarbons on Partially Acetylated Cellulose—II

T. M. Spotswood

J. Chromatography, 3 (Feb 1960) 101-110

Techniques described in Part I for separation of polycyclic aromatic hydrocarbons by chromatography on acetylated cellulose have been supplemented by introduction of alternative methods of locating compounds on the developed chromatogram by the isolation in crystalline form of extracts from paper chromatograms. By improved acetylation techniques, papers of increased resolution power and better mechanical properties could be obtained. The separations on partially acetylated paper were reproduced on larger scale using columns of partially acetylated cellulose powder together with the same solvent systems. Mixtures such as 3,4-benzopyrene, perylene, 3,4-benzofluoranthene, 10,11-benzofluoranthene, 1,12-benzofluoranthene, 1,12-benzoperylene and 2,3,10,11-dibenzoperylene could be resolved into constituents by this method without appreciable overlap of fractions as would occur in alumina columns. F.J.

Identification of Organic Compounds. XXIX—Paper Chromatography of Di- and Triphenylmethane Dyes

J. Gasparić and M. Matrka

Collection Czechoslov. Chem. Commun., 24 (1959) 1943-9 (in German)
Chem. Abs., 53 (25 Oct 1959) 19393

4,4'-Methylenebis(N,N'-dimethylaniline), Michler's hydroly, Michler's ketone, bis[4,4'-bis(dimethylamino)benzhydrol]ether, 4,4'-bis(diethylamino)benzhydrol, 4'-dimethylamino-4'-diethylaminotriphenylcarbinol, Auramine O (C.I. Basic Yellow 2), Auramine G (C.I. Basic Yellow 6), Doebner's Violet and its leuco base, Malachite Green base, chloride, perchlorate, oxalate, leuco base (C.I. Basic Green 4, C.I. Solvent Green 1), Brilliant Green (C.I. Basic Green 1), Setoglaucine O (I), Turquoise Blue Extra B (II), Methyl Violet (C.I. Basic Violet 1), Parafuchsin and its leuco base (C.I. Basic Red 9), Crystal Violet and its leuco base (C.I. Basic Violet 3), Methylene Green (C.I. Basic Green 5), Fuchsin (C.I. Basic Violet 14), New Fuchsin (C.I. Basic Violet 2), Victoria Blue B (C.I. Basic Blue 26), Aniline Blue B and Night Blue (C.I. Basic Blue 15) were chromatographed on Whatman No. 3 impregnated with a 2, 5, and 10% solution of dodecyl alcohol in ethyl alcohol. The developing agents used were ethylalcohol-aq. ammonia (1:1) and ethylalcohol-aqueous ammonia-water (2:2:1). The dyes travelled as neutral colourless compounds having no affinity for cellulose; various salts of the same dye thus have the same *R_f* value (demonstrated in the case of Malachite Green, its chloride, perchlorate, and oxalate). I, II, and C.I. Basic Violet 1 are not homogeneous and so form several spots. Doebner's Violet, Parafuchsin, Malachite Green, and Crystal Violet were separated from their residual leuco bases by paper chromatography on Whatman No. 4 impregnated with HCONH₂ and using benzene as developer: the dyes remain at the origin whereas the leuco bases and other intermediates present travel in front of the mobile phase. This makes the procedure suitable for determining the residual bases in oxidation dyes. C.O.C.

Reverse-phase Chromatography of Solvent Dyes

M. R. Verma, R. Dass, and J. Rai

Current Sci. (India), 28 (1959) 148
Chem. Abs., 53 (10 Nov 1959) 19517

Solvent dyes can be resolved by using paper impregnated with paraffin and either of two solvents: 70% vol./vol. acetone in water or acetone:pyridine:water, 25:10:40. C.O.C.

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Detection of Reduction Products of Azo Basic and Acid Dyes by Paper Chromatography

S. Kitahara, S. Miyazaki, and H. Hiyama

Kogyō Kagaku Zasshi, 61 (1958) 189-193
Chem. Abs., 53 (10 Nov 1959) 20809

A number of dyes were reduced with hot Sn-HCl or Zn-HCl and then paper chromatographed at 20°C. using butanol-HCl (4:1 by vol.) or 2% HCl as the developer and NW-acid or FeCl₃ as the colouring agent. The colour and R_f values of the following dyes are tabulated and success in identifying the reduction products is claimed: Chrysoidine (C.I. Basic Orange 2), Bismarck Brown G (C.I. Basic Brown 1), Janus Red B (C.I. 26115), Paracin Scarlet A, Sunchromine Brown RH (C.I. Mordant Brown 33), Metanil Yellow (C.I. Acid Yellow 36), Methyl Orange (C.I. Acid Orange 52), Orange I (C.I. Acid Orange 20), Orange II (C.I. Acid Orange 7), Acid Orange RO, Paracin Chrome Violet, Diamond Black, Chroserine, Amaranth (C.I. Acid Red 27), Acid Brilliant Scarlet 3R (C.I. Acid Red 18), Chrome Yellow MD, Silk Scarlet (C.I. Acid Red 9), Chrome Blue Black FZ, Methyl Red (C.I. Acid Red 2), Solar Blue Black (C.I. Acid Black 1), Solar Cyanine GR (C.I. Acid Blue 116), Acid Cyanine 5R (C.I. Acid Blue 120), Sunchromine Black F 120 (C.I. Mordant Black 5), Tartrazine (C.I. Acid Yellow 23), Chrome Orange GR (C.I. Mordant Orange 6), Acid Red PG (C.I. Acid Red 85), Acid Red RS, Sunset Yellow FCF (C.I. Food Yellow 3), Acid Anthracene Red 3B (C.I. Acid Red 89), Acid Alizarin Red G (C.I. Mordant Red 17), Supranol Red BB (C.I. Acid Red 154), Supranol Orange GS (C.I. Acid Orange 33), Paracin Fast Orange GN, Paracin Fast Yellow GRN, Paracin Fast Yellow ELN, Sulfon Yellow R (C.I. Acid Yellow 42), Supramine Yellow R (C.I. Acid Yellow 25), Supramine Blue R (C.I. Acid Blue 117), Victoria Fast Violet B (C.I. Acid Violet 27), Supranol Fast Bordeaux B (C.I. Acid Red 134) and Anthracene Red (C.I. Mordant Red 8). Silk dyed with these dyes was similarly reduced and the reduction products successfully identified by paper chromatography.

C.O.C.

Critical Examination of the Permeability Method for Determining the Specific Surface of Pigments

F. Kindervater

Deut. Farben-Z., 8 (1959) 312-7

Chem. Abs., 53 (10 Nov 1959) 20832

Carman's permeability method (*Chem. Abs.*, 32 (1951) 6009) depends on the porosity of the pigment which to yield maximum surface must be in the 0.4-0.5 range. Measurements of specific surface by this method on ZnS (C.I. Pigment White 7), Lithopone (C.I. Pigment White 5), and silica (C.I. Pigment White 27) are only 70-80% of the values obtained by the Brunauer, Emmet and Teller method (*Chem. Abs.*, 32 (1938) 4037) and only 55-60% of those for anatase and rutile (C.I. Pigment White 6). Electron microscope measurements indicate that the permeability method measures a kind of geometric surface.

C.O.C.

Chromatography of Flavonoid Pigments

J. B. Harborne

J. Chromatography, 2 (Nov 1959) 581-603

A review of techniques used in paper partition chromatography, of naturally occurring flavones, flavanols, flavanones, isoflavones, chalcones, and aurones, together with a short section on column chromatography. R_f values of their glycosides and aglycones and some methylated derivatives are given. Sections include separation purification and identification by chromatography, the relationship between certain aspects of structure and R_f values, and chromatographic methods used in the classification of natural distribution of flavonoid pigments. 91 references.

F.J.

Identification of Unknown Synthetic Fibres. Part III—Revision and Application of Micro Fusion

S. G. Smith

Amer. Dyestuff Rep., 48 (26) (28 Dec 1959) 23-6

A revised scheme to include the latest fibres. It uses micro fusion in addition to observations of fibre morphology, behaviour under polarised light, optic sign, refractive index, and solubility. A systematic method is given for identifying 25 man-made fibres by group separation and confirmatory tests.

C.O.C.

Electronic Moisture Gauge for Running Tyre Yarn

G. J. Hilferink

Rayon Revue, 23 (1) (Nov 1959) 34-9

An electronic single-thread moisture gauge suitable

for use both in the laboratory and in the works, e.g. for warps coming from a drier.

C.O.C.

Measurement of Moisture Content of Moving Fabrics

O. König

Textil Praxis, 14 (Dec 1959) 1250-1256

After reviewing conventional methods of measuring moisture content of textile fabrics in motion (based on electrostatic potential, dielectric constant, and electric conductance) a new measuring system developed from first principles is described. The portable instrument consists of two parts joined by a cable. Two earthing electrodes and a contact electrode are mounted on a condenser plate, and this part is placed manually in contact with a moving fabric. The second component contains an anode battery, two potentiometers, and a galvanometer which indicates directly the moisture content irrespective of the fabric's speed and thickness.

L.A.T.

A New Method of Test for Yarn Slippage in Woven Fabrics

L. S. Veer

Rayon Revue, 23 (1) (Nov 1959) 17-27

Determining Covering Power for Leather of Dyes and Pigments

D. Kokeš and K. Motýčka

Věda a výzkum v průmyslu kožedělném, 4 (1958) 65-76

Chem. Abs., 53 (25 Oct 1959) 19421

A 0.1% dispersion of the colorant in casein is gradually added to a vessel through which passes light from a stabiliser-fed 60 w. bulb, filtered by ground glass, on to a photocell galvanometer unit. Volumes are compared at 20% decrease in transmission of light. There is an inverse exponential relationship between the concentration of colorant and transmission of light about this value. Results are reproducible within 2%. In addition glass discs were weighed, sprayed with a 5-15% dispersion or solution of the colorant, dried, and weighed. Light transmission was measured in a similar apparatus. Log of the ratio of light transmission to weight of colorant was reproducible only to 5% but compared somewhat more favourably with tests on leather.

C.O.C.

Identification of Food Dyes by means of the Complex formed with Quaternary Ammonium Compounds

B. Drevon, A. Cier, P. Laroumagne, and J. Laur

Congr. soc. pharm. France, 9^e, Clermont-Ferrand (1957) 279-284

Complexes formed from various quaternary ammonium salts with food dyes can be separated chromatographically on alumina impregnated paper. The spots are developed with iodine-bismuth reagent. With hexadecylcyclohexyl ammonium bromide particularly good separation of the dyes is obtained.

C.O.C.

Separation and Identification of Artificial Colours authorised by the Italian Hygiene and Sanitation Commission 23rd Dec. 1957 for use as Food Dyes

R. De Gori and F. Grandi

Boll. lab. chim. provinciali (Bologna) 9 (1958) 276-286

Chem. Abs., 53 (25 Oct 1959) 19189

A mixture of seven dyes is separated by extraction with ether and paper chromatography. They are identified spectrophotometrically. The first chromatogram made on circular paper SS 2043/A using as solvent 15 ml. methanol, 30 ml. water and 0.2 g. MgCl₂·6H₂O, yields two distinct circular zones after 4 hr. The inner zone contains Azorubine (C.I. Food Red 3) and Amaranth (C.I. Food Red 9), the outer Scarlet GN (C.I. Food Red 2), Fast Red E (C.I. Food Red 4), Victoria Scarlet Red, and Ponceau 6R (C.I. Food Red 8). Ether extracts Erythrosine (C.I. Food Red 14) from an aqueous solution of the dyes acidified with acetic acid. The two zones are separated by eluting with water. Ascending chromatography of each group using SS 2043/A and as solvent 25 ml. water, 25 ml. butanol, and 20 ml. ether, completely separates the dyes each having, respectively, R_f : 0.41, 0.12, 0.69, 0.59, 0.28, and 0.10 E/E_{max} and the characteristic curve are also given for each dye.

C.O.C.

Synthetic Food Colours

I—Characteristics and Properties of the Water-soluble Dyes approved for use in Spain

R. G. Olmedo and L. Villanúa

Anales bromatol. (Madrid), 11 (1) (1959) 9-47

Reviews the characteristics, chemical and toxicological properties and applications of 4 yellow, 12 red, 6 blue,

3 violet, 2 green, and 1 orange dye allowed to be used in food or on food wrappers in Spain.

II—Spectrophotometric Study of the Water-soluble Dyes

A. Carballido and L. Villanúa *Ibid.*, 49-108
Describes the constitutions, classification, and light absorption curves of the above dyes.

III—Spectrophotometry of Water-soluble Red, Orange, and Yellow Dyes at various pH

Ibid., 109-178
Chem. Abs., 53 (25 Oct 1959) 19190
Absorption maxima at various pH are given. C.O.C.

New Reflectometer and Its Use for Whiteness Measurement

R. S. Hunter *J. Opt. Soc. Amer.*, 50 (Jan 1960) 44-8
A new 0°-45° blue- and green-light reflectometer has S-4 vacuum phototubes in a ratio-measuring circuit. Where whiteness is of interest, materials are usually yellowish in hue. In such cases, precise reflectance measurements with just the blue and green tristimulus filters are adequate for whiteness determination. Investigators have found that, in general, yellowness detracts much more from perceived whiteness than does greyness. For best correlation with visual gradings, the green-minus-blue reflectance difference corresponding to yellowness should receive 4-5 times the weight of luminous (green) reflectance alone. Because inadequate blue reflectance detracts so strongly from perceived whiteness widespread use is now being made of blue fluorescing dyes on textiles, paper, and plastic. These fluorescent brightening agents absorb in the near ultraviolet and fluoresce in the blue. An ultraviolet-absorbing filter in the new instrument may be alternated between the sample-viewing and incident light beams to include and then exclude the near-ultraviolet. This makes possible measurement of the contribution of the fluorescent brightening agent to blue reflectance, and thence to whiteness. C.O.C.

Convenient Colour Indices for Near-white Samples

E. Allen *J. Opt. Soc. Amer.*, 49 (Dec 1959) 1227-8
A method using Source C illumination and two readings either with a photoelectric colorimeter or a spectrophotometer which enables easy calculation to give results directly in NBC (Judd) units. C.O.C.

Hysteresis and Related Textile Properties. II—A Counting Tube System Resilience Meter

K. Shirakashi, K. Ishikawa, W. Ishibashi, and T. Shibusawa *J. Soc. Textile Cellulose Ind. Japan*, 15 (Nov 1959) 863-867

The load, applied to a magnetostriction type strain gauge, can be transformed into voltage. The rectified output, A.C. voltage, is applied to the grid of the reactance tube, which forms part of the oscillator. The input voltage is changed to a frequency in proportion to that voltage. The frequency is converted into pulses and integrated by a dekatron. The apparatus need not be confined to small deformations, and hysteresis, resilience, and toughness after large deformations resulting from repeated elongations can be measured. Diagrams and details are given of the electric circuits including the switching, deformation, and heating mechanisms. L.P.

T.T.S. No. 57. Quantitative Chemical Analysis of Binary Mixtures of Cellulose Triacetate and Certain Other Fibres

J. Textile Inst., 50 (Dec 1959) p 754-8

T.T.S. No. 58. Quantitative Chemical Analysis of Mixtures of Cellulose Triacetate and Secondary Cellulose Acetate Fibres

J. Textile Inst., 50 (Dec 1959) p 759-762

Tests for Distinguishing between Nylon 66 and Perlon dyed with Logwood Black

M. Stratman *Z. ges. Textil-Ind.*, 61 (1959) 427-430
Chem. Abs., 53 (10 Nov 1959) 20813

Use of aqueous $ZnCl_2$ -I solution with alcohol is unsatisfactory. Dimethyl formamide which normally dissolves Perlon but not nylon has little action on either fibre containing 2% Logwood Black (C.I. Natural Black 3). The two dyed fibres can be distinguished by the lactophenol test in which nylon is unaffected but Perlon swells, first at the ends which become cup-shaped and later throughout the whole fibre. C.O.C.

T.T.S. No. 59. Method of Test for the Measurement of the Pore Size of Fabrics (Bubble Pressure Test)

J. Textile Inst., 50 (Dec 1959) p 763-7

Interlaboratory Trial of the Pore Size (Bubble Pressure) Test

J. Lord *J. Textile Inst.*, 50 (Dec 1959) p 768-p 771

T.T.S. No. 60. Method of Test for the Determination of Stiffness of Cloth

J. Textile Inst., 50 (Dec 1959) p 772-5

T.T.S. No. 61. Determination of the Tensile Properties of Individual Textile Fibres and Filaments

J. Textile Inst., 50 (Dec 1959) p 776-p 782

New Waterproofness Tester for Gloving Leathers

R. G. Mitton and F. R. Morgan
J. Soc. Leather Trades Chem., 44 (Jan 1960) 32-41

The apparatus, which is fully described with the aid of a photograph and two diagrams, is based upon that described by Mann (*J. Amer. Leather Chem. Assoc.*, 51 (1956) 377). The test-piece is pressed intermittently against a stationary wet surface, simulating the conditions experienced when gloves are worn in wet weather; there is good agreement with practical glove trials in which wet bricks were picked up, but no significant correlation with any other laboratory test for waterproofness. J.W.D.

A Simple and Inexpensive Glossmeter

D. S. Newton
J. Oil. Col. Chem. Assoc., 43 (Jan 1960) 44-5

Details are given of a glossmeter devised to overcome the difficulties which arise when the gloss on an exposed panel is measured after a period of dull weather and/or by different observers. C.O.C.

Simple and Rapid Colour Reaction for Distinguishing Methyl Methacrylate Resins from Acrylate Resins

E. N. Mano *Anal. Chem.*, 32 (Feb 1960) 201

A test giving good results with many methacrylate and acrylate resins and monomers from many sources is to depolymerise a 0.5 g. sample in a test tube while preventing escape of monomer vapours by a piece of filter paper fixed with the clamp that holds the tube. To the condensed monomer in the test tube add a few ml. of nitric acid (s.g. 1.40) and heat gently over a small flame. The solution becomes yellow. Cool, add half its volume of water and then zinc powder. The solution becomes blue immediately if methacrylate resin is present in the sample. This blue is easily extracted by chloroform, the chloroform extract being a deeper blue than the original solution. The yellow component first formed is not extracted by chloroform. Excess zinc turns the solution colourless. The solution also becomes blue if $NaNO_2$ is used instead of zinc. C.O.C.

Photochemical Destruction of Fabrics and of their Protective Finishes

N. V. Kalugin
Tekhnol. tekstil. prom., No. 4 (11) (1959) 17-22

Samples of grey water-proof and combined water- and rot-proof tent cloths were sealed in quartz and glass tubes in an atmosphere of air, O_2 , N_2 , H_2 , or in *vacuo* and exposed to daylight for long periods (e.g. 300 days). From determinations of strength losses it is concluded that (a) ultraviolet radiation causes an overall greater strength loss, (b) heat, generated through light absorption, has the greatest destructive effect on the combined water- and rot-proof samples, (c) the action of light on the protective proof is an initial destruction of the fibre, with subsequent desorption of the finish by water. G.J.K.

Detection of Wool Damage

K. Wegjan and H. G. Fröhlich
Text. Research J., 30 (Jan 1960) 73-74

It is shown that simultaneous determination of alkali solubility and alkaline thioglycollate extraction constitutes a means of distinguishing between acid and oxidation damage. S.B.D.

Identification of Synthetic Dyes used in the Italian Food Industry

G. Ceresa *Ann. sper. agrar. (Rome)* 13 (1959) 545-571
Chem. Abs., 53 (25 Nov 1959) 22553

The 13 food dyes permitted in Italy are identified readily and with certainty by one-dimensional paper chromatography using ethanol:butanol:water (50:25:50) as developer. Those dyes not completely separable by this

mixture can be separated by $N-HCl$ or by adding 10 ml. conc. NH_4OH to 100 ml. of the above mixture. R_f values are given for the dyes in each developer. C.O.C.

Paper Chromatographic Detection of the Food Dyes Officially Permitted in Taiwan

H. Y. Hsu and M. T. Wang

Taiwan Pharm. Assoc., 10 (1958) 2-10 (in English)
Chem. Abs., 53 (25 Nov 1959) 22551

A study of one-dimensional ascending paper chromatography for analysis of 23 permitted food dyes, 6 non-permitted basic dyes and 140 samples of coloured confectioneries. C.O.C.

The Pycnometric Determination of Pigment Density and its Accuracy

K. Řeháček

Deut. Farben-Z., 13 (1959) 347-354
Chem. Abs., 53 (25 Nov 1959) 22987

ASTM D153-54 Methods A and B fail to take account of the effect of temperature differences on the accuracy of determining d . Thus, variation of $\pm 0.5^\circ C$. gives a maximum calculated error of 2.3%. Incomplete deaeration and refilling of the pycnometer and insufficient temperature equalisation of its contents are major factors. The pigment volume must be $\leq 2\%$ of that of the pycnometer. A 50 ml. conical pycnometer with capillary stopper gives less than 0.25% error if the temperature is controlled within $\pm 0.1^\circ C$. C.O.C.

A Simple Test for Determining the Dye Penetration of Fabrics

E. Nestelberger

Textil Praxis, 15 (Jan 1960) 53-55

A crockmeter is used with a piece of dyed fabric with carborundum paper of medium grain instead of the white test piece on the instrument head. The appearance of the abraded area indicates the extent of dye penetration. An arbitrary scale of 5 standards is used for the assessment of results. L.A.T.

Wash and Wear Fabrics—Appearance after Home Laundering

AATCC Tentative Test Method 88-1958

Amer. Dyestuff Rep., 47 (25 Aug 1958) 578-580

Quantitative Estimation of Cotton in Cotton-Rayons Blends

E. Frieser

Textil Praxis, 15 (Feb 1960) 160-168

A comprehensive report with experimental details is given of the chief methods extant for the above determination. It includes 10 chemical processes (based respectively on calcium thiocyanate, caustic soda by the Schwartz and Zimmerman procedure and its modification by Schwertassek, sulphuric acid, sodium zincate, Heim's sodium zincate-ammonium thiocyanate procedure, formic acid-zinc chloride and a modification by Marschall and V. Schlütter, and finally formic acid-calcium chloride and a modification by Marschall (cf. *Kunststoffe und Zellulose*, 22 (1940) 215), the latter depending on the reduced sensitivity to acids produced on cotton by formaldehyde, the gelatin process (microscopic) of Herzog, and separation of the mixture components by sedimentation. It is now established that the modified formic acid-calcium chloride procedure of Marschall (*loc. cit.*) gives the most accurate results, the components being separated by the quantitative dissolution of the rayon from the insoluble (rendered) cotton. H.H.H.

Testing Cotton Cordages for Resistance to Attack by Micro-organisms. IS 1959:1386

Indian Standards Institution

Detection and Estimation of Damage in Cotton Fabrics caused by Micro-organisms. IS 1959:1316

Indian Standards Institution

Decomposition of Cellulose in Cotton Fibre by the Black Aspergilli

M. E. Simpson and P. B. Marsh

Plant Disease Repr., 43 (1959) 1042-7
Chem. Abs., 53 (25 Nov 1959) 22207

Aspergillus niger has been deemed to be a non-cellulose-decomposing organism but when unbleached cotton cloth containing a little glucose is incubated with this organism then cellulose decomposition occurs. Several of the truly black *Aspergilli* closely related to *A. niger* behaved similarly. Isolates of purple-black *Aspergilli* of the *A. luchuensis* series caused loss in strength of the cloth in absence of glucose. C.O.C.

Methods for Detection of Siroset Treatment in Wool Fabrics

T. Gerthsen and H. Zahn

J.S.D.C., 75 (1959) 604-605

Quantitative Estimation of Protein Rayons in Mixture Yarns

E. Frieser

Textil-Rund., 15 (Feb 1960) 65-74

Qualitative differences within the fibre class are discussed and quantitative methods based on $NaOH$, $NaOCl$, $Ba(OH)_2$, $CH_3COOH-ZnCl_2$, trypsin, pepsin, and H_2SO_4 are detailed. The distribution of amino-acids in some protein synthons and results of analyses of known mixtures are given. S.R.C.

Identification of Unknown Synthetic Fibres. Part III—Revision and Application of Micro Fusion

S. G. Smith

Amer. Dyestuff Rep., 48 (26) (28 Dec 1959) 23-6

The qualitative analysis of man-made fibres by light microscopy described in Parts I and II (J.S.D.C., 74 (1958) 619; 75 (1959) 510) has been revised to deal with the latest fibres. The method now uses micro fusion in addition to observations of fibre morphology, behaviour under polarised light, optic sign, refractive index and solubility. A systematic method is given for identifying 25 synthetic fibres by group separation and confirmatory tests. C.O.C.

The Determination of Colour Fastness to Dry-heat Pleating and Setting

S.D.C. Heat Treatments Subcommittee

J.S.D.C., 76 (March 1960) 158-168

Determination of the Air Permeability of Fabrics

J. Lord

J. Textile Inst., 50 (Oct 1959) T 569-582

Describes an instrument which gives good reproducibility of results. The flow of air is proportional to pressure with closely woven fabrics but, with more open fabrics, is more nearly linearly related to the square root of the pressure. Flow is proportional to specimen area within the limits studied. Resistances to airflow of multi-layers of fabric are additive. C.O.C.

Colour Reaction for Methacrylate (Monomer and Polymer)

E. B. Mano

Anal. Chem., 32 (Feb 1960) 291

Ca. 0.5 g. of the sample is depolymerised in a test tube and a few ml. conc. HNO_3 (s.g. 1.40) added to the condensed liquid. After cooling, half the volume of water is added and a little Zn powder. The solution turns blue immediately if methacrylate resins are present. P.B.S.

Detection and Analysis of Chlorosulphonated Polyethylene

G. G. Esposito

Offic. Digest. Fedn. Soc. Paint Technol., 32 (Jan 1960) 67-70

A qualitative test is to dissolve 10 mg. nonvolatile in 3 ml. pyridine and add 25 mg. 2-fluorenamine when presence of chlorosulphonated polyethylene is indicated by formation of a reddish orange or red. Vinyl chloride-vinyl acetate copolymer, neoprene, chlorinated rubber, alkyls, epoxy, polyurethane, cellulose nitrate, and oils are negative to the test. Sulphur and chlorine can be determined by $K_2CO_3-Na_2O_2$ fusion. Total solids of the system before curing are obtained by weighing a sample of 5-10 g., immediately after stirring, into a tared 80 mm. flat container, drying at $110^\circ C$. for 3 hr., cooling, weighing and calculating the amount of nonvolatile. The residue left is kept for pigment analysis. It should not be ignited to remove organic accelerator present as to do so may produce erroneous results with some methods of analysing pigments. C.O.C.

Methods of Testing Vulcanised Rubber

BS 903: Parts B11 and B12:1960. Rubber (Polymer)

Determinations (replacing Part 4 in BS 903:1950)

British Standards Institution, Price 6s.

Covers the following methods—Part B11—Calculation of rubber (polymer) content; Part B12—Determination of rubber (polymer) content; Section 1 Natural rubber hydrocarbon, Section 2 Nitrogen (for acrylonitrile copolymers), Section 3 Chlorine (for chloroprene polymers and copolymers), Section 4 Total hydrocarbon rubber (for natural butadiene-styrene and butyl rubbers). Gives details of reagents, apparatus, procedure, and expression of results. C.O.C.

Variations in the Assessment of Light-fastness Exposures

K. McLaren

J.S.D.C., 75 (1959) 597-599

Xenon-arc Fading Lamps

K. McLaren

J.S.D.C., 75 (1959) 594-596

Tests for Colour Vision

F. Jordinson and T. Minshall

J.S.D.C., 75 (1959) 585-593

Defective Colour Vision. Comparison of a Colour Vision Test made from Dyed Wool Patterns with the Ishihara Test

J. G. Wain

J.S.D.C., 76 (March 1960) 181-184

PATENTS

Determining the Particle Size Distribution of Fine Powders

Pillsbury Mills

BP 828,757

Inexpensive apparatus for readily measuring by sedimentation, according to Stokes's law, the particle size distribution of a fine powder. C.O.C.

Sample Holder for making Test Dyeings

Ciba

BP 827,577

The container for the sample has a perforated base, impermeable side walls, and a movable perforated cover. This cover is adjustable to any height within the container but is always below the top of the side walls. C.O.C.

Monitoring the Colour of a Liquid

Proctor & Schwartz

BP 819,484

The strength of a dyebath can be controlled by passing one beam of light through a standard and another beam of light through a sample of the dye liquor which is continuously by-passed from and into the main bath. A number of limited frequency bands are sequentially selected simultaneously from both light beams before they pass through the standard in order to compare the standard and sample at different frequencies. After passing through the standard and sample the light beams are continuously compared to detect deviation from their predetermined relative intensities existing when the sample matches the standard. C.O.C.

Moisture-determining Apparatus for Regenerated Cellulose Film

American Viscose Corp.

BP 827,773

Apparatus in which the moisture content of the film is determined on the basis of its degree of stretch under instantaneous or gravity loading conditions. C.O.C.

Characterisation of Vegetable Dyes by Paper Chromatography (IV p. 247)**New Pigment-mixture Diagram and Colour System (V p. 249)****Relation between Dye Absorption and Cotton Fibre Properties at Equilibrium (VI p. 250)**

XV— MISCELLANEOUS

Planning for Cost Improvement in Dyeing and Finishing**Part I**

W. G. Leslie

Dyeing and Finishing Symposium, Melbourne, 1959, pp. 111-4

Deals with the rôle of the accountant in the industry.

Part II

P. J. Maclellan

Ibid., 115-125

Deals with the efficient use of labour, machines, and materials. Stock-taking, steam consumption, and work study are also discussed. C.O.C.

Light Sources and Colour Rendering

D. Nickerson

J. Opt. Soc. Amer., 50 (Jan 1960) 57-69

Light sources for many problems in industry require good colour rendering: standards are needed for both special and general purpose lamps. Target standards are discussed, and colour, relative spectral distributions, and lumen efficiency data are given for typical incandescent fluorescent lamps. Data for colour samples calculated for triads of light sources studied by an I.E.S. Subcommittee on Colour Rendition of Light Sources are used to demonstrate the comparative size and direction of colour differences involved in common situations. Problems raised by chromatic adaptation are discussed, as are specifications and standards for sources used for colour

work in various specialised industries, and the progress being made by I.E.S. and C.I.E. committees on colour rendering. C.O.C.

Formulation of Transparent Colours with a Digital Computer

F. W. Billmeyer, J. K. Beasley, and J. A. Sheldon

J. Opt. Soc. Amer., 50 (Jan 1960) 70-2

A digital computer was programmed to calculate the concentrations required to produce a given transparent colour by mixing soluble dyes. The computation was based on Beer's law calculations at 65 wavelengths across the visible spectrum. The computer formulation technique was tested by making a series of mixtures of dyes according to a computed formula in a solvent and in an acrylic resin. Correspondence was good between the measured colours of the mixtures and those for which the formulations were calculated. C.O.C.

The Education of ChemistsT. L. Cottrell *J. Roy. Inst. Chem.*, 84 (Feb 1960) 57-62

In this Inaugural Lecture to the University of Edinburgh on 20 Nov. 1959 the author asserts at the outset that the so-called experiments in chemical education are simply changes of teaching method or material without any rigorous attempt to follow up the results of the change. He next outlines what a University is for, and then discusses how it should cope for a situation in which about 72% of the 21,000 qualified chemists in Great Britain are engaged in applied chemistry, 4% in academic teaching and research and the remainder in work determined by the above two groups. Of the 72%, a little more than half are engaged in research and development, and the rest on production, selling, sales service, and general management; there is also a supporting staff of 1½ persons per chemist. The author opines that most industrial chemists lack professional competence because of three defects—lack of power to apply theory, inability to make a critical approach to the problem in hand, and inability to communicate (i.e. write) clearly. He also notes that wide or deep reading in chemistry is only attempted by the exceptional student, and suggests that time for thought should be obtained by a drastic reduction (by about half) in the time spent in laboratory work, since pure manipulative skill should have relatively little effect on the rating of a student as a potential chemist. Doubt is expressed as to how much information is understood from lecture courses, and the formulation of a minimum amount of knowledge is recommended—cramming should be avoided. The time thus rendered available should be spent in discussion, whereby critical thought and reading could also be fostered by essays, i.e. the standard procedure in an Arts Faculty. Practical exercises in difficult calculations could profitably replace many of the laboratory experiments, and finally a research problem should be tackled which has been carefully chosen to prevent the student becoming a mere technician for his research supervisor. The views advanced are for the education of the majority, but creative powers should be recognised and encouraged when encountered, since genius cannot be produced by formal education. H.H.H.

PATENTS

Water-repellent Finish on Non-porous Surfaces

Bradford Dyers' Association Ltd.

BP 825,551

The process described in BP 809,822 (*J.S.D.C.*, 75 (1959) 271) is also applicable to non-porous surfaces, e.g. rubber, synthetic resins, cellulose acetate, metals, ceramics, and glass. C.O.C.

Coloured Wire

United States Steel Corp.

USP 2,900,710

Rod from which wire is to be drawn is cleansed and then a base coating applied by dipping it into an aqueous suspension of lime, a carbonate, phosphate, borate, silicate, TiO₂, chromates or MgO. From 1-12 dips may be necessary. After this coating is dried the rod is dipped into an aqueous solution of a dye. This may be repeated several times, the rod being dried between each immersion. The number of times the rod is dipped in the dye liquor depends on the vividness of colour and the coverage desired. Dyeing is carried out at atmospheric temperature except for the last dip when the rod is flash baked at 450°F. for 5 min. The coloured rod is then drawn in the usual manner to yield a coloured wire. C.O.C.

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APPOINTMENTS VACANT

THE GOUROCK ROPEWORK CO. LTD., Port Glasgow, manufacturers and producers of ropes, nets and canvas, have a vacancy in their Research Department for a Textile Technologist. Applications are invited from persons of the 20-25 age group with qualifications in H.N.C., A.T.I. or A.S.D.C. standard. Some experience in general textile technology with a bias towards the chemical side is desirable. Excellent conditions of employment. Staff pension fund. Apply to Chief Chemist, The Gourock Ropework Co. Ltd., Port Glasgow, Renfrewshire.

WILLIAM HOLLINS & COMPANY LTD., makers of "Vivella" and "Vivella", have a vacancy in their Central Training Department, Plessey Vale, near Mansfield, for a dyeing technologist to take charge of the merchandise serviceability section. Candidates should preferably have full City and Guilds, A.T.I. or A.S.D.C., but practical experience in all branches of colour fastness assessment would be essential. Salary will be commensurate with qualifications and experience and the Company operates an excellent contributory superannuation scheme.

Application should be made in writing to: The Personnel Officer, William Hollins & Company Ltd., Vivella Mills, Plessey Vale, Mansfield, Nottinghamshire.

WORKS CHEMIST required for PRINT WORKS in North of England. Applicants should be aged 25-25 years and hold H.N.C. or equivalent. Previous experience of Printing, Processing and Laboratory work essential. This position offers good prospects to the successful applicant.

Replies, which will be treated as confidential, should state age, qualifications, experience and salary required. Advertiser's staff notified. Box V280

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The Organisation's Division of Textile Industry, Geelong, Victoria, (Official Research Laboratories) invites applications from Honours graduates in Science or Textile Science (or equivalent qualifications) with at least two years appropriate research experience for a position as Physicist or Chemist. The Division is concerned with improvements in existing wool textile processes and development of new techniques. The appointee is required either to investigate chemical research on the modification of wool involving effects such as shrink proofing and sericin resistant finishes; or to participate with physicists on the study of wool processing, particularly the development of new approaches to present methods of processing.

SALARY—Dependent on qualifications and experience within the range—£A1,510-£A2,185 p.a.

Salary for a female will be £A100 p.a. less than corresponding male rates.

Promotion within C.S.I.R.O. is by merit and may ultimately go beyond the upper limit of the scale within which the original appointment is made. Dr. H. Lippson, Chief of the Division, will be available in England during May for interview and discussion.

Fares paid. Further details of conditions, etc., supplied on application to—

Mr. E. J. Drake, Chief Scientific Liaison Officer, Australian Scientific Liaison Office, Africa House, Kingsway, London, W.C.1.

to whom applications (quoting Appointment No. — 464/195) should be addressed by the 14th May 1960.

MISCELLANEOUS

THE Proprietors of British Patents Nos. 720440 and 721333 are prepared to sell the patents or to license British manufacturers to work thereunder. They relate to "Preparation of Liquid Indophenol Sulfurized Dyestuffs" and "Concentrated Ready-to-Dye Liquid Sulfur Dyestuffs" respectively. Address—BOULT, WADE & TENNANT, 112 Hatton Garden, London E.C.1.

JOURNALS WANTED

THE Society is urgently wanting Journals (in good condition) for January and February 1960.

Please address communications to the General Secretary.

Nominal payment will be made.

NEW MEMBERS

Barker, J. J., The Silsden Dyeing Co. (1915) Ltd., Silsden, Yorkshire
Bates, R. F., 8 Oaklands Road, Northenden, Manchester 22
Beever, D. K., Ashton House, 13 Thornton Crescent, Morecambe, Lancashire
Bernardi, G. A. De, Via G. Espinasse 3, Busto Arsizio (Varese), Italy
Berryman, D. W., Balm Paints Pty. Ltd., P.O. Box 60, Clayton, Victoria, Australia
Brighton, D. A., Vinyl Products Ltd., Butter Hill, Carshalton, Surrey
Cardwell, A. A. B., "Bettony", Greenway Gardens, Braintree, Essex
Cochett, E. F., 912 Wheeler Avenue, Box 830, Rte. 6, North Charleston, S. Carolina, U.S.A.
Crawford, R., Tennants Textile Colours Ltd., c/o Tennants (Lancs) Ltd., Hazel Bottom Road, Manchester 8
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Stafford, Miss A., 60 Forknell Avenue, Wyken, Coventry
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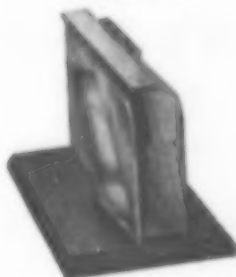
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by Charles Hugh Giles Ph.D F.R.I.C F.S.D.C

Senior Lecturer in Chemical Technology
Glasgow Royal College of Science and Technology

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